The use of Atomic Force Microscopy to determine intermolecular adhesive forces in wood based composite materials

by

Bernard Effah

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Supervisor: Prof. Martina Meincken

Co-supervisor: Prof. Albert Van Reenen

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Declaration

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Abstract

South Africa has considerable invasive wood species that are causing damage worth millions of dollars to the national economy every year. These species cover over 8 % of surface area and needs to be cleared from public land. Finding potential use for this inexpensive, unexploited and abundantly available raw material regarded as waste and incorporating them into wood plastic composites (WPCs) as wood fillers can provide substantial value adding to a waste material, whilst producing products with good performance properties. The aim of the study was to comprehensively characterise the interfacial interaction forces and properties of LDPE - Wood composites with different compatibilisers and different wood species.

The first part of the study discussed thoroughly issues of WPCs, as well as the Atomic Force Microscopy (AFM) and how the latter can be used to characterise the individual components of the composite to gain a better understanding of what affects good interfacial adhesion and how that could be maximised; most especially the use of chemical force microscopy (CFM) as the basic concept for the study.

In the second part, the tip-surface interaction forces between two different wood species and AFM tips modified with three different compatibilisers were mapped to show the varying compatibility between the components of WPCs. Force maps and histograms were used to identify and show potential compatibiliser binding sites on the wood substrates.

In the third part, chemically functionalized tips were used to quantify the adhesive force between compatibiliser coated AFM tips, the polymer and the different wood substrates and the result related to macroscopic properties of WPCs in an attempt to understand and explain the mechanical properties as well as to determine the feasibility to use alien invasive wood species for the production of WPCs with the most suitable compatibiliser.

The final part of the study focused on the physical and mechanical properties of WPCs made from LDPE, six invasive wood species and three different compatibilisers. Thus, the moisture content, density, tensile modulus, tensile strength, elongation at break and impact strength were analysed and the results compared to commercial WPCs to ascertain the technical feasibility of the physical and mechanical properties of WPCs made from the invasive species.

Quantitative analysis using one-way ANOVA with Tukey post hoc test and regression model were used to determine significant differences and relationships. The study proved that CFM is capable to characterise the surface structure, chemical functionalities of the different components and localise as well as also quantify functional groups and therefore give an indication of their adhesive forces on a molecular scale. The incorporation of PE-g-MA and dPE compatibilisers improved adhesion and thus enhanced the tensile properties of the composite. The measured properties compared very well to those of commercial WPCs. Finally, the invasive wood species that were studied can be incorporated into WPCs, by using the right compatibiliser. Furthermore, thermally degraded LDPE presents a new and inexpensive compatibilizer that can replace traditionally used expensive compatibilisers, in many cases with superior properties.

Opsomming

Suid-Afrika het 'n aansienlike hoeveelheid indringende hout spesies wat jaarliks skade ter waarde van miljoene dollers aan die nasionale ekonomie veroorsaak. Hierdie spesies dek meer as 8% van oppervlakte en moet uitgerooi word vanaf openbare grond. Potensiële gebruike vir hierdie goedkoop, onontginde en oorvloed beskikbare grondstowwe wat as afval beskou word en inkorporering daarvan in hout plastiek samestellings (WPCs) as hout vullers kan aansienlike waarde toevoeg tot 'n afvalmateriaal, tesame met die vervaardiging van produkte met goeie eienskappe. Die doel van die studie was om die tussenvlak interaksie kragte en eienskappe van LDPE-hout samestellings met verskillende versoeningsmateriale en verskillende hout spesies volledig te karakteriseer.

Die eerste deel van die studie bespreek deeglik die kwessies van WPCs, asook die atoomkrag mikroskopie (AFM) en hoe laasgenoemde gebruik kan word om die individuele komponente van die samestelling te karakteriseer en 'n beter begrip te kry van wat goeie tussenvlak adhesie beïnvloed en hoe hierdie gemaksimeer kan word; veral die gebruik van chemiese krag mikroskopie (CFM) as die basiese konsep vir die studie.

In die tweede deel is die punt-oppervlak interaksie kragte tussen twee verskillende hout spesies en AFM punte, gemodifiseer met drie verskillende versoeningsmateriale gekarteer om die verskillende versoenbaarheid tussen die komponente van WPCs te wys. Kragkaarte en histogramme was gebruik om potensiële versoeningsmateriaal bindingsplekke op die hout substrate te identifiseer en te wys.

In die derde deel was chemies gefunksionaliseerde punte gebruik om die adhesiekrag tussen versoeningsmateriaal bedekte AFM punte, die polimeer en die verskillende hout substrate te kwantifiseer en die resultaat gekorrileer met makroskopiese eienskappe van WPCs in 'n poging om die meganiese eienskappe te verstaan en verduidelik asook om die haalbaarheid van die gebruik van uitheemse hout spesies te bepaal vir die produksie van WPCs met die mees geskikte versoeningsmateriaal.

Die finale deel van die studie het gefokus op die fisiese en meganiese eienskappe van WPCs bestaande uit LDPE, ses indringende houtsoorte en drie verskillende versoeningsmateriale. Die

voginhoud, digtheid, trek modulus, treksterkte, verlenging tydens breek en impaksterkte is ontleed en die resultate vergelyk met kommersiële WPCs om die tegniese haalbaarheid van die fisiese en meganiese eienskappe van WPCs vervaardig van die indringersoorte te bepaal.

Kwantitatiewe analise met behulp van eenrigting ANOVA met Tukey post hoc toets en regressiemodel is gebruik om betekenisvolle verskille en verwantskappe te bepaal. Die studie het bewys dat CFM in staat is om die oppervlak struktuur en chemiese funksionaliteite van die verskillende komponente te karakteriseer asook die kwantifisering van funksionele groepe en dus 'n aanduiding van hul adhesie kragte op 'n molekulêre vlak gee. Die inkorporering van PE-g-MA en dPE versoeningsmateriale het gelei tot beter adhesie en dus ‘n verbetering in die trek eienskappe van die samestelling. Die gemete eienskappe het baie goed met dié van kommersiële WPCs vergelyk. Ten slotte kan die indringer hout spesies wat bestudeer is in WPCs inkorporeer word deur gebruik te maak van die regte versoeningsmateriaal. Verder bied termies gedegradeerde LDPE 'n nuwe en goedkoper versoeningsmateriaal wat tradisioneel gebruikte duur versoeningsmateriale kan vervang, in baie gevalle met uitstaande eienskappe.

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List of Abbreviations/Glossary

AFM	Atomic force microscopy
AIS	Alien invasive species
ANOVA	Analysis of variance
CFM	Chemical force microscopy
dPE	Thermally degraded LDPE
DMSO	Dimethyl sulfoxide
DMTA	Dynamic mechanical thermal analysis
EDX	Energy dispersive x-ray analysis
EVA	Ethylene-vinyl acetate
EVOH	Ethylene vinyl alcohol
F/D	Force distance
FTIR	Fourier transform infrared spectroscopy
LDPE	Low density polyethylene
nN	Nanonewton
PE	Polyethylene
PE-g-MA	Polyethylene-graft maleic anhydride
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
PVC	Polyvinyl-chloride
RH	Relative humidity
SAMs	Self-assembled monolayers
SEM	Scanning electron microscope
SNOM	Scanning near-field optical microscopy
STM	Scanning tunneling microscope
TEM	Transmission electron microscope
VDW	Van der Waals
WPCs	Wood plastic composites
wt%	Weight percent
XPS	X-ray photo-electron spectroscopy

List of publications

Publication I

Effah B, van Reenen A, Meincken M (2015) Characterisation of the Interfacial Adhesion of the Different Components in Wood-Plastic Composites with AFM. *Springer Science Reviews*, 3(2), 97-111.

Publication II

Effah B, van Reenen A, Meincken M (2016) Localisation and quantification of potential binding sites for compatibilisers on soft- and hardwood in wood-plastic composite systems. *Surface and Interface Analysis*, DOI 10.1002/sia.6189.

Publication III

Effah B, Raatz K, van Reenen A, Meincken M (2016) Chemical Force Microscopy Analysis of Wood Plastic Composites Produced from different Wood Species and Compatibilisers. *Wood and Fiber Science*, reviesed version submitted.

Publication IV

Effah B, van Reenen A, Meincken M (2016) Mechanical properties of wood-plastic composites made from various wood species with different compatibilisers. *European Journal of Wood and Wood Products*, reviesed version submitted.

List of conference contributions

Presentation I

Effah B, Raatz K, van Reenen A, Meincken M (2016) Adhesive forces acting between the components of wood-plastic composites on molecular and macroscopic scale. 13th Pacific Rim Bio-Based Composite Symposium. 13th to 15th November, Concepcion, Chile.

Presentation II

Effah B, van Reenen A, Meincken M (2016) Mapping of functional groups on wood surfaces with Atomic Force Microscopy. Microscopy Society of South Africa Conference. 5-8 December, Boardwalk Convention Centre, Port Elizabeth, South Africa.

Chapter One

Introduction

1.1 Background

Contemporary consensus on the environmental footprint of materials has renewed societal interest in the development of newer materials that can reduce stress on the environment (Baillie 2004). Similarly, unstable petroleum prices, eminent shortage and pressure for decreasing the dependency on petroleum and plastic products have caused an increasing interest to maximize the use of renewable materials like wood (Kim and Pal 2010). This has in recent times brought into existence an array of wood based composite materials, which transformed the area of material technology to meet the growing population of the world (Babu et al. 2009). Wood plastic composites (WPCs) are thermoplastically processible composites made from renewable biomass materials, plastics and additives. Of the biomass materials, wood is the most commonly used material (Vogt et al. 2005). Wood is not the only natural fibre used in WPCs, but it is the most commonly used (Williams and Bauman 2007). The filler elements may be fibres, particles, flakes, wafers, strands, veneers, or sawn lumber from wood resources (Gillespie 1981). The matrix polymers are typically low-cost commodity polyolefins that flow easily when heated, allowing for considerable processing flexibility when wood is combined with them (Clemons 2008).

The use of wood particles as reinforcing agents in thermoplastics has indeed opened up a new avenue for the utilization of waste fibers, which are abundantly available in nature. WPCs were developed over the last 40 years, resulting in increased applications and an expanded market share (Schwarzkopf and Burnard 2016). WPCs are relatively new products when compared to the long history of natural lumber, or traditional wood composites, such as particleboard or fibreboard. Predominantly, the WPC market is dominated by rail and decking products in North America, while in Europe the emphasis is in automotive applications. In China and other parts of Asia the WPC market is experiencing considerable growth in a wide variety of products (Smock 2011). WPCs are also increasingly used to produce furniture, technical parts, consumer goods and household electronics using injection moulding and other processes (Dammer et al. 2013).

WPCs have become useful materials with superior qualities to natural wood in several ways: the thermoplastic polymer component resists rot and insects, thus providing an inherently longer product life and less maintenance requirement than wood alone (Williams and Bauman 2007; Klyosov 2007). The cellulosic fibres provide reinforcement and increase the rigidity of the product compared to the polymer component. WPC products can be worked like wood using the same tools and fastening techniques and they can be pigmented during processing for long-lasting colour, or painted after installation (Tangram 2002; Markarian 2005). Additionally, the variation of various properties found in wood between species, trees and even pieces from the same tree, are not inherent in WPCs as the properties can largely be determined and controlled during processing (Youngquist 1999).

Nevertheless, one important drawback of WPCs is the chemical incompatibility between hydrophilic wood fibers and the hydrophobic thermoplastic matrices. This incompatibility at the interface results in reduced adhesion, which limits the reinforcement potential of the fibers. The adhesion properties of the individual components of WPCs determine their compatibility and determine their physical and mechanical properties. To overcome the incompatibility, a compatibiliser is often used to improve interfacial bonding of the two different phases (Youngquist 1999; Caulfield et al. 2005; Rowell 2007; Sain and Pervaiz 2008; Kim and Pal 2010). It is known that the mechanical properties of WPCs depend strongly on the interfacial adhesion between the components and this can be maximized by improving the interaction and adhesion between the two phases in the final composites (Klyosov 2007; Farsi 2012). Compatibilising is a technique utilising the electrostatic nature of the two different materials to bridge the surfaces (Satov 2008). The primary function of compatibilisers is to improve the blend homogeneity of dissimilar or incompatible materials. Inhomogeneity may prevent the development of satisfactory structural properties in the end product and the use of compatibilisers improves the properties of WPCs (Satov 2008). Commonly used product(s) include poly(ethylene-co-vinyl alcohol) (EVOH) and poly(ethylene-graft- maleic anhydride) (PE-g-MA), which have been used to modify the polymeric matrix and improve the interfacial strength and subsequently the mechanical properties of WPCs (Farsi 2012). The ethylene in EVOH interacts with the polymer matrix and the hydroxyl group bonds to the wood surface. PE-g-MA is also composed primarily of ethylene, which attaches to the non-polar polymer matrix and maleic anhydride grafted onto it to bond to the wood surface.

The behaviour of WPCs is best explained on the basis of the combined behaviour of the reinforcing element, the matrix and the interface. Adhesion describes the contact of the two elements at the interface so that mechanical force can be transferred across the interface (Ebnesajjad 2008; Pocius 2012). The mechanical force that is needed to separate both elements from one another is called adhesion force or pull-off force (Israelachvili 2011). In theory, the work of adhesion upon separation of surfaces is defined by the surface energy and interfacial surface tensions of the interacting materials (Israelachvili 2011; Pocius 2012). There is no single theory of adhesion, which can satisfactorily explain all the interactions between an adhesive and a substrate. Nonetheless, of the various adhesion mechanisms found in literature, mechanical interlocking, adsorption /diffusion theory and the formation of a boundary layer can be applied to WPCs (Kim and Pal 2010). When the adhesive force is weak, adhesion failure may occur at the interface between the wood fibres and polymer matrix in WPCs (Kim and Pal 2010; Stokke et al. 2013).

To achieve better mechanical properties, the interfacial adhesion should be strong, as the mechanical properties of WPCs depend highly on the stability of the interface (DiBenedetto 1981; Gillespie 1981). The strength of WPCs is determined by the strength of the fibres and by the ability of the matrix to transmit stress to the fibres. The transmission of stress to the filler particles is affected by the aspect ratio, fiber or particle orientation, geometry and the interfacial bond between fibre and matrix (Baillie 2004; Stokke et al 2013). In order to promote high performance and long term stability, it is necessary to form strong, chemically stable interfaces between the fiber and plastic components (DiBenedetto 1981). Wetting and fibre dispersion in the polymer matrix are of great importance in achieving good adhesive interaction between two phases. Wetting in WPCs is characterised by the degree of direct interfacial contact between the wood and polymer surface. Dispersion on the other hand is the degree of mixing in the WPC system.

The properties of WPCs are therefore affected by many factors: the choice of raw materials, the fibre content and the processing parameters (Baillie 2004). Additionally, successful formulation of WPC products depends on overcoming problems, such as the influence of moisture, unfavourable chemical interactions of adhesive and matrix, morphology of the components, stability under ambient and varying conditions and cost (Oliver 2013). The final properties of WPC to a large extent also depend on the compounding and processing conditions and as such the effective mixing of the individual components is vital for achieving optimal dispersion of wood fiber and optimizes the properties of WPCs (Kim and Pal 2010).

It must be emphasised that the quality of WPCs depends to a large degree on the wood properties and preparation of wood surfaces for successful bonding. Similarly, the adhesion properties of the polymer surface are crucial for adhesive bonding and composite manufacturing, as the final product performance and the efficiency of stress transfer depends on the surface properties of the raw materials (Gourianova et al 2005; Tshabalala 2005).

With the recent development of various advanced surface characterization techniques, the understanding of material surfaces has been significantly improved making it possible to control and tailor surface characteristics for specific applications from micrometers down to molecular scale. In this regard the atomic force microscope (AFM) is a valuable tool to examine surfaces at high resolution. It allows the analysis of topography, distribution of heterogeneous materials and mechanical properties of materials. AFM has proven to be an appropriate and reliable method for the investigation of adhesion phenomena (Gourianova et al 2005) through the measurement of force/distance curves. The AFM system images a surface by means of a sharp probe, situated at the apex of a flexible cantilever, which is normally formed from silicon or silicon nitrite (Magonov and Whangbo 1996; Amelinckx et al. 1997; Leite and Herrmann 2005). Visualization of specific structures, qualitative and quantitative measurements of local mechanical and chemical identification of surfaces with AFM techniques is an invaluable way of material surface characterization (Prater et al. 1995; Starostina and West 2006).

Traditionally, WPC production has focused on the use of few selected wood species – mostly softwoods with long, uniform tracheids (Fabiyi and McDonald 2010), which result in good reinforcement of the polymer matrix. Most polymers on their own are not suitable for load-bearing applications, due to their lack of sufficient strength, stiffness and dimensional stability (Ebewele 2000; Mohanty et al. 2005) and therefore need fibres to serve as reinforcement to the polymer matrix (Mohanty et al. 2005).

In South Africa, alien invasive species (AIS), are species that were introduced from other countries and tend to out-compete the original vegetation. Although many alien species are essential for human survival and wellbeing, the harmful effects of invasive alien species are widely recognized (Richardson and Pyšek 2004). These species have become more prevalent and contribute to environmental and ecological problems, like increased fire danger, topsoil erosion, reduced ground water and reduced stream flows (Nyoka 2003; Macdonald et

al. 2003; Clemons and Stark 2007). There are 200 species of plants declared as weeds or invaders, of which 121 are woody species in South Africa (Biodiversity explorer 2016). Several of these species have to be removed from land by law and are commonly used as firewood with very little value adding. They are therefore regarded as waste material and using them as raw material for WPCs can be considered as an environmentally friendly way of value adding to a waste material.

1.2 Objectives of the study

Wood plastic composites (WPC) are regarded as a value adding opportunity for wood and plastic waste, as efficient resource utilisation, hazardous fuel removal from forests and the utilisation of small diameter logs, wood residues and machining co-products. WPC production can be carried out with almost no waste, an improvement for the timber and plastic industries, which have to deal with large amounts of off-cuts and plastic waste, respectively. WPCs are an important and growing segment of the forest products and plastic industries. To meet the industrial, commercial and environmental demands on WPCs the product performance must be continuously improved, especially the inherent incompatibility of wood and plastic, which affects the adhesion between the two components.

This study aims to comprehensively characterise the interfacial interaction forces and properties of LDPE-wood composites with different compatibilisers and different wood species. The first part of the study discusses WPCs in general, as well as Atomic Force Microscopy (AFM) and how the latter can be used to characterise the individual components of the composite to gain a better understanding of what affects good interfacial adhesion and how this can be maximised.

In chapter four, the compatibiliser/wood interaction forces were investigated and quantitatively mapped with AFM, using chemically modified tips to detect potential binding sites of compatibilisers on various wood surfaces.

In chapter five, the molecular interaction forces determined with chemical force microscopy (CFM) were correlated to macroscopic physical and mechanical properties. The study also explained the macroscopic mechanical properties with the microscopic adhesive characteristics.

In chapter six, the study evaluated the mechanical properties of WPCs made from LDPE, various invasive wood species from South Africa and three different compatibilisers. The tensile strength, tensile modulus, elongation at break, hardness and impact strength were analysed to determine the feasibility of utilizing alien invasive species for the production of WPCs, as well as the use of a new compatibiliser based on degraded LDPE.

A general materials and methods section detailing all experiments in closer detail is presented after the introduction chapter. The nature and extent of the main author's contribution to the publications and the nature and extent of the contribution of the co-authors and supervisors is provided in an appendix at the end of the thesis.

1.3 Thesis layout

This dissertation is structured as a cumulative work of published articles, which are presented below:

Chapter 3

Characterisation of the Interfacial Adhesion of the Different Components in Wood-Plastic Composites with AFM. Effah B, Van Reenen A and Meincken M (2015), Springer Science Reviews, 3(2), 97-111.

Chapter 4

Localisation and quantification of potential binding sites for compatibilisers on soft- and hardwood in wood-plastic composite systems. Effah B, Van Reenen A and Meincken M (2016). Surface and Interface Analysis.

Chapter 5

Chemical Force Microscopy Analysis of Wood Plastic Composites Produced from different Wood Species and Compatibilisers. Effah B, Raatz K, Van Reenen A and Meincken M, (2016) revised version submitted to Wood and Fiber Science.

Chapter 6

Mechanical properties of wood-plastic composites made from various wood species with different compatibilisers. Effah B, Van Reenen A and Meincken M, (2016) revised version submitted to European Journal of Wood and Wood Products.

The format of the publications appearing in Chapters 3-6 was maintained as the format required by the journals.

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Chapter Two

Materials and Methods

This chapter describes in detail all materials and methods used in the experimental work, which have been described in the publications more briefly and those that were not reported in the publications.

2.1 Materials

LDPE from Sasol Polymers (South Africa) with a melt flow index of 65 g/10 min and polypropylene (Sigma-Aldrich; Isotactic, average Mw-12 000, and Mn-5 000) were used as matrix polymers and to produce model films.

The compatibilisers were poly(ethylene -vinyl-co- alcohol) (EVOH) with 44 mole% ethylene and poly(ethylene-graft-maleic anhydride) (PE-g-MA), obtained from Sigma-Aldrich and thermally degraded LDPE (dPE), which was supplied by the Department of Chemistry and Polymer Science (Stellenbosch University). Irganox + PP_{02}_1 stabiliser from Sasol Polymers was added to all WPC formulations. The polymers and compatibilisers were used as received for further processing.

The wood was sourced from six invasive tree species, namely *Pinus radiata* (pine), *Eucalyptus grandis* (eucalyptus), *Acacia mearnsii* (black wattle), *Acacia longifolia* (long-leaved wattle), *Acacia saligna* (Port Jackson) and *Casuarina cunninghamiana* (beefwood). The wood was supplied by the Department of Forest and Wood Science (University of Stellenbosch).

Extractives were obtained from pine (softwood) and eucalyptus (hardwood) in the Department of Forest and Wood Science at Stellenbosch University.

2.2 Preparation of specimens

2.2.1 Extractive preparation

Extractives were removed from softwood (pine) and hardwood (eucalyptus) by means of Soxhlet extraction according to Tappi standard T 264 om-88. A sample of 5 g of milled and dried wood of each species was placed in a paper extraction thimble, which was placed in

position in the Soxhlet apparatus on the top of a clean, dry and weighed 500 mL round bottom flask containing 200 mL of distilled water or a mixture of ethanol/cyclohexane (1:2). The Soxhlet extraction was carried out by boiling water reflux overnight. In order to determine the amount of extractives, water or ethanol/cyclohexane was evaporated from the 500 mL flask. Subsequently, the flask was dried in an oven at 103 ^{o}C overnight, and the percentage of extractives determined based on the weight of the oven dry flask.

2.2.2 Preparation of degraded LDPE

An unstabilised LDPE was degraded in a vacuum oven at 90 °C for 5, 7, and 9 weeks to functionalise the LDPE. The formation of new and additional functional groups was monitored by FTIR spectroscopy on a regularly basis. This resulted in the degraded polyethylene (dPE) compatibiliser.

2.2.3 Model films

Model films of wood components were prepared from solution and pellets by direct deposition and film casting of lignin alkali, α-cellulose, softwood and hardwood extractives, PE-g-MA, EVOH, dPE, LDPE and PP, respectively. The lignin alkali was dissolved in deionised water (Kimix chemicals) and deposited on a glass substrate. For the cellulose film, a mixture of α -cellulose (1.33 g, 8.21 mmol based on glucose units) and 50ml *N*,*N* dimethylacetamide (DMAc) (Kimix chemicals) was heated to 150 °C for 30 min in a round bottomed flask equipped with a condenser. Then LiCl (1.08 g, 25.5 mmol) was added and the mixture was heated to 166 °C for 8 min. The reaction mixture was subsequently cooled to room temperature and stirred overnight for dissolution. This solution was then directly deposited on a glass substrate and dried in oven at 40 °C for 4 hours. PE-g-MA, PP and LDPE were dissolved with xylene and deposited on glass substrates. EVOH was dissolved with dimethyl sulfoxide (DMSO) (Kimix chemicals) by heating at 120 °C and deposited on glass substrate. The extractives were deposited on glass substrates and dried in oven at 40 °C for 4 hours. dPE was cast on a glass substrate after heating to 120 °C.

All samples were stored in a desiccator until testing. The deposition of solutions was performed by dropping the solution on the inclined substrate and subsequent drying.

Five films were produced from each solution and the best film was selected for AFM analysis.

2.2.4 FTIR analysis

FTIR spectroscopy was carried out using a Nicolet Is10 FTIR spectrophotometer operated in the absorption mode, in the wave number range of 4000-400 cm^{-1}. The spectra were obtained using a resolution of 4 cm^{-1} and averaged over 32 scans. Omnic software was used for data acquisition and analysis to determine the functional groups of the films.

2.2.5 Preparation of Wood Flour

The wood was debarked, after which it was chipped with a chipper and further milled in a Drotsky hammer mill with a 4 mm screen. It was then dried in an oven at 103 °C ± 2 for 24 hours. Size screening of the particles was done in a Retsch shaker (AS 200). Particles retained in the 180 μm sieve were used for the composites.

2.2.6 Particle size

The wood particles were suspended in water and spread on a glass slide. After drying the length and width of 250 randomly selected particles were measured with a Leica EZ 4D optical microscope using the Leica Application Suite (LAS) software at 20x magnification.

2.2.7 Preparation of Wood sections

Blocks of clear wood with the dimensions of 15×15×15 mm^3 were prepared from all six wood species. The samples were kept in a conditioning room at 20 °C at a relative humidity of 60% for two weeks, after which 20-40 μm thick sections were cut along the grain with Leica RM 2245 rotary microtome with a 16 cm steel blade.

2.2.8 Wood pH

The pH value of the wood was determined by cold extraction and measured with a PH 25+ meter (Crison Instruments, S.A). One g of the milled sample (40 mesh) was soaked with 70 ml distilled water in a 100 ml beaker. The mixture was stirred with a magnetic stirrer and allowed

to soak for 1 hour at room temperature, before submerging the electrode to record the pH value. The pH meter was calibrated pior to measurements in three standard solutions (pH 4.0, pH 7.0 and pH 10.0).

2.2.9 Preparation of functionalised AFM tips

Attachment of COOH and CH_3 groups

Silicon force modulation cantilevers from Nanosensors (Switzerland) were coated by Novascan Technologies (Ames, IA USA) with COOH and CH_3 groups.

Attachment of EVOH, PE-g-MA and dPE groups

Silicon force modulation cantilevers from Nanosensors (Switzerland) were used for the tip modification according to Bastidas et al. (2005), Maver et al. (2011), Berquand and Ohler (nd), Klash (2010) and Basson (2013). Tips terminating with the following functional groups were prepared:

- EVOH

- PE-g-MA

- dPE (Degraded LDPE).

The silicon tips were first coated with gold using an Edwards S150A Gold Sputter Coater and cleaned under a 254 nm UV lamp for 1 hour to ensure that all organic material was removed. A 1 mM solution of 11-mercapto-1-undecanol, 1-octadecanethiol and11-mercapto undecanoic acid (all from Sigma-Aldrich, used as received) in ethanol (KIMIX) was prepared. The gold tips were submerged in the thiol solution and allowed to react for 2 hours at room temperature under Argon gas. A 2 mM PE-g-MA solution was prepared in xylene at elevated temperature of 40 °C, and then allowed to cool. A 2 mM EVOH solution was prepared with DMSO (KIMIX). A 2 mM dPE solution was prepared in xylene at elevated temperature of 40 °C, and then allowed to cool. The thiol coated tips were allowed to react with the PE-g-MA, EVOH and dPE solutions individually for 2 hours to prepare functionalized tips terminating with PE-g-MA, EVOH and dPE respectively. The coated tips were then rinsed with n-heptane (KIMIX) and alcohol, and dried in an argon stream.

2.2.10 Preparation of WPCs

In a pilot study, composites with varying amounts of wood and compatibiliser were prepared with pine as a reference species, in order to determine the optimum wood loading and compatibiliser ratio for each compatibiliser. The wood content was 30, 40 and 50 wt% and the compatibiliser ratios were 5, 7 and 10 wt % of the polymer part. Stabilizer (2 wt% of the polymer part) was added to prevent degradation. The optimum polymer/wood ratios were found to be 70/30 with 7% EVOH compatibiliser, 70/30 with 10% dPE compatibiliser and 50/50 with 10% PE-g-MA compatibiliser. These ratios were maintained for all other wood species.

Composite samples of 5 g total mass were compounded in two replicates by dissolving the LDPE in 80 mL xylene at 140 °C and then adding the stabiliser and wood flour into the solution, while stirring on a hot plate. The solution was stirred and cooled to room temperature, which was followed by precipitation in acetone. The samples were then filtered (150 ml Buchner funnel filter; Sinta Glass) and allowed to dry in a constant air flow at room temperature for three days and conditioned.

2.2.11 Injection molding

Samples were molded into tensile bars (“dog bone” shaped) with a HAAKE Mini Jet II from Thermo Scientific (type 557-2290) according to ASTM D638 (ASTM 2010). Five tensile bars of each composite were prepared for tensile, hardness and impact resistance testing. The samples were conditioned in a climate chamber at 20 ± 3 ºC and relative humidity of 65 % prior to testing.

The samples had dimensions of 15.26 mm length, 3.03 mm width and 0.76 mm thickness. Pure LDPE was used as control to ascertain the performance of the compatibilisers. The following settings were used: Cylinder temperature (180 ºC), mold temperature (90 ºC), injection pressure (250 bar) and post hold pressure (250 bar).

2.3 Sample Characterisation

2.3.1 AFM imaging and adhesive force determination

In the first stage, the interaction forces between polar (-COOH) and non-polar (-CH_3) functional

AFM tips on films of individual wood components, namely lignin, cellulose and extractives, the matrix polymers LDPE and PP and the compatibilisers PE-g-MA, EVOH, dPE were investigated to mimic either the polar wood surface, or the non-polar polymer surface, which serve as the basis of our concept.

For the main CFM measurements and analysis reported in the publications, an Easy Scan 2 AFM from Nanosurf (Switzerland) was used in the force modulation imaging, force mapping and spectroscopy modes. Force modulation cantilevers with a 2 N/m spring constant from Nanosensors were used and the tips were chemically modified. Adhesive force-distance curves were obtained, and were used to determine adhesive forces between chemically modified tips and α-cellulose, lignin, extractives, polymers, compatibilisers and wood surfaces. All AFM measurements were carried out in air at ambient conditions. In order to achieve results describing the entire sample with statistical relevance, enough curves were measured at different positions on each sample and outliners eliminated to determine the average adhesive force between the modified tip and sample surface. The resulting force maps were created with the imaging software SPIP (6.0.14 and 6.2.0).

2.3.2 Physical properties

The moisture content of each WPC after conditioning for several weeks at 20 ºC and 65% RH was measured by the oven-dry method according to ASTM D-4442 (ASTM 2007) using equation 1:

$$MC\ (\%) = \frac{Initial\ mass - ovendry\ mass}{ovendry\ mass} \times 100 \qquad (1)$$

The basic density was determined by volume measurement in accordance with ASTM D-2395 (ASTM 2014) and calculated with equation 2:

$$\rho = \frac{ovendry\ mass}{green\ Volume} \times 100 \qquad (2)$$

2.3.3 Mechanical characterisation

2.3.3.1 Tensile tests

The tensile strength was determined on an LRX (LLOYD instruments) tensile tester. No preload was applied at a cross-head speed of 50 mm/min. At least five dumbbell shaped samples were analysed for each WPC formulation to obtain average values. Tensile modulus, tensile strength and elongation at maximum load were calculated from the stress / strain curves and average values with standard deviations reported.

2.3.3.2 High speed tensile impact test

A CEAST Torino (6546/000) high speed tensile impact tester was used to study the impact strength of the composite samples. The composite samples were subjected to a 15 Joule hammer weight (type 0.96) at a 90° angle. Five samples were tested to report the average impact strength.

2.3.3.3 Hardness

A Shore D Durometer (0 - 100) micro hardness tester was used to analyse the hardness of the samples at a dwell time of 15 seconds. Fifteen measurements were obtained per sample to calculate the average hardness values.

2.4 Statistical Analysis

Statistical analysis was conducted using the Origin 8.5.1 software. Mean values with error bars representing 95% confidence intervals were plotted for all the tests in combination with a one-way analysis variance (ANOVA). A Tukey HSD Test was used to test the statistical significance at 0.05 % probability level. To understand the relationship among the variables, correlation and regression analysis were conducted.

Chapter Three

Characterisation of the Interfacial Adhesion of the Different Components in Wood Plastic Composites with AFM

Summary

Over the last few years, wood plastic composites (WPCs) have received considerable attention from the wood and plastic industries due to growing environmental issues, increasing cost of raw materials and the demand for eco-friendly composite materials. Generally, WPCs consist of cellulosic fibers, a matrix polymer and compatibiliser. Commonly, the fiber- matrix adhesion in WPCs is improved by using compatibilisers that bond to the polar wood fibers and the non-polar polymer matrix. Understanding the adhesion mechanism between cellulosic fibers and the compatibiliser, as well as between the compatibiliser and the polymer is a requisite for predicting the strength properties of WPCs. The first part of this study served as thorough literature review of WPCs and Atomic Force Microscopy (AFM) and how the latter can be used to characterise the individual components of WPCs to gain a better understanding of what affects the interfacial adhesion and how it can be optimised.

With the recent development of various advanced surface characterization techniques, the understanding of material surfaces has been significantly improved making it possible to control and tailor surface characteristics for specific applications from micrometers down to molecular scale. AFM is a scanning probe microscope technique that investigates and measures surface structure with high resolution and accuracy by scanning a probe over a sample surface to build up a map of the topography of the surface. AFM has also proven to be an appropriate and reliable method for the investigation of adhesion phenomena through the measurement of force/distance curves. The ability of AFM to create 3D, high resolution images of surface morphology, as well as interaction forces, has made it an essential tool for material characterisation in general. Specifically, for WPCs this technique can potentially be very useful, as they typically consist of three different components and their mechanical properties depend strongly on the interfacial adhesion between all three of them. AFM can be used to characterise the surface structure, as well as chemical functionalities of the main components and localise and to a degree quantify functional groups and therefore give an indication of the adhesive

forces on a molecular scale. The high resolution of AFM also makes it possible to localise measurements that take heterogeneous fibre into account and can potentially explain why certain components work in some cases better than others. For example, not all compatibilisers work equally well on all wood fibers and studying the interfacial adhesion between different compatibilisers and different wood fibers with AFM can help to understand this phenomenon.

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SYSTEMATIC STUDENT REVIEW

Characterisation of the Interfacial Adhesion of the Different Components in Wood Plastic Composites with AFM

Bernard Effah[1] Albert Van Reenen[2] Martina Meincken[1]

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Abstract The search for innovative solutions for the reuse of solid residues has intensified with growing environmental issues and the increasing cost of most raw materials, leading to the design of eco-friendly composite materials, such as wood–plastic composites (WPCs). These materials combine the stability of wood fibres with the durability of plastic, allowing for a wide range of applications, whilst simultaneously offering the possibility of utilising waste products from the forest/wood industry and recycled plastic. Waste products that otherwise incur cost for disposal therefore become a sustainable material resource for new products. Natural fibres offer a number of advantages over synthetic fibres and are seen as a ''green'' alternative to other reinforcements. Commonly, the fibre-matrix adhesion in WPCs is improved by using compatibilisers that bond to the polar wood fibres and the non-polar polymer matrix. However, the problem with these is that good dispersion is not always achieved as it depends on the adhesion properties of three individual components in the WPC, which might lead to poor mechanical properties of the WPC. The ability of the atomic force microscope (AFM) to create 3D images of topography and various interaction forces with molecular resolution made it a valuable tool for the analysis of adhesion properties in WPCs.

Keywords Natural fibres · Composites · Compatibiliser · Sustainability · AFM

Endorsed by Martina Meincken.

Bernard Effah
18761569@sun.ac.za

Albert Van Reenen
ajvr@sun.ac.za

Martina Meincken
mmein@sun.ac.za

[1] Department of Forest and Wood Science, Stellenbosch University, Stellenbosch, South Africa

[2] Department of Chemistry and Polymer Science, Stellenbosch University, Stellenbosch, South Africa

Introduction

In recent times, increased environmental awareness throughout the world has led to an increasing interest in natural fibres and their applications in various fields [87]. This has in turn led to the development of completely new composite materials by combining different resources in such a way that a synergism between the components results in a new material that is better than the individual components. With this in mind, the World Commission on Environment and Development in 1987 observed that ''the time had come for a marriage of the economy and ecology'' [90].

Composite materials are made from two or more materials with significantly different physical or chemical properties, which remain separate and distinct within the finished structure [47, 58]. Composites are used in areas such as automotive, building, appliances, packaging and biomaterials [58, 75, 80]. Composites can be classified based on the matrix, which could be metal, ceramic or polymers [3, 80]. The classifications according to the type of reinforcement are particulate composites, fibrous composites and laminate composites. The classification can even include the types of fibres used [39].

Natural fibres offer a number of advantages over traditional synthetic fibres and are widely used for the

production of wood–polymer composites or wood–plastic composites (WPCs) [47, 80]. In the composite industry, natural fibres are seen as a ''green'' alternative to reinforcements of other sources. Economically, the use of plant co-products for composite production avoids the use of new agricultural lands, which limits competition with alimentary products and also becomes sources of remuneration to farmers [7]. Plastic is found in all sectors of human life and the attitude of people towards the excessive use and careless disposal of the plastic has led to a drastic environmental pollution. Similarly, a large amount of wood waste is generated at different stages in the wood processing industry and a large proportion of the waste is either incinerated or deposited in landfill sites. On the other hand, the growing production and consumption of plastic worldwide has resulted in the development of waste recycling facilities, which produce the raw material for another generation of plastic products [80]. Furthermore the search for innovative solutions for the reuse of solid residues increased in the late 20th century and has intensified with growing urgency for environmental preservation [53] leading to the design of eco-friendly materials including WPCs [75].

Wood Plastic Composites

Wood–polymer or WPCs are a relatively new class of materials that covers a broad range of composite materials utilising an organic resin binder (matrix) and fillers composed of cellulosic material [58]. These rapidly developing materials for high technology products possess the advantage of utilising waste products from the forestry industry and recycled plastic from household waste. Waste products that would usually incur cost for proper disposal, therefore become a new material resource, allowing recycling to be both profitable and environmentally sustainable. Polymers like polypropylene (PP), polyethylene (PE), polyester, epoxy and polyvinyl chloride (PVC)—the latter mainly in the US—have an established status in composite applications. Natural fibres can originate from wood, agricultural plants and residues, grasses, water plants and a wide variety of waste agromass including recycled wood, paper and paper products [11].

Matoke et al. [59] emphasised the growing interest in the use of natural cellulosic fibres as the reinforcement for polymeric matrix and noted that, adding natural powder or fibre to plastics provides a cost reduction to the plastic industry and improves the physical and mechanical properties of the composite. For the production of high performance wood composites, a fundamental understanding of the properties of the materials involved is essential [89].

Two major constituents make up WPCs: the fibres and the matrix. The interface between the fibre and matrix is critical for the function of the composite material and as such could be added as a third constituent of the material [35, 49]. Many complex phenomena including matrix phase separation, development of chemical bonds, interdiffusion and physical interactions combine to transfer loads at the interface and lead to durable materials with excellent mechanical properties [48]. Information about the behaviour of the fibre/matrix interface can directly be obtained at the microscopic scale using micro-mechanical analysis, such as pull-out, microbond or fragmentation tests [50].

Like any other advanced product, a WPC has its own complications, especially the interfacial adhesion between the polar wood fibres and the non-polar polymer, which is normally very poor and therefore depends on coupling agents to initialise the bond [47, 98]. Wood is a hydrophilic porous composite of cellulose, lignin and hemicellulose, which are rich in functional groups like hydroxyl groups. On the other hand, many matrix polymers are hydrophobic, with very few functional groups. This incompatibility results in non-uniform dispersion of fibres within the matrix leading to poor mechanical properties. In order to improve the affinity and adhesion between fibres and polymer matrix in production, chemical compatibilising agents are normally employed [43]. The primary function of a compatibiliser is to form an interphase between the wood and the plastic, as such the compatibiliser should have a domain or functionality that is compatible with the wood fibre, as well as a domain that is capable of interacting with the polymer matrix [69]. The compatibilisers are added in small quantities to form a bridge between the otherwise incompatible materials. They act via the formation of covalent bonds, secondary bonding, polymer molecular entanglement or mechanical interlocking [52]. The type and level of compatibiliser for WPCs should be carefully selected in order to produce composites with acceptable properties and performance [69].

To improve reinforcement and mechanical properties, such as strength and stiffness, the fibres need to be well dispersed within and well bonded to the matrix. If at a certain location, the fibres are not properly bonded to the matrix, delamination and void formation will occur. In such situation stress transfer between fibre and matrix would fail and these locations could serve as nucleus for cracks to form [11].

The major factors to determine the properties of WPCs are fibre dispersion, fibre length distribution, fibre orientation and fibre-matrix adhesion [47, 70, 80]. Poorly dispersed fibres could lead to agglomeration or the formation of voids, which should be avoided to produce efficient composites.

Wood and Other Natural Fibres Used in WPC

The term WPC refers to any composite that contains wood of any form and either thermoset or thermoplastic polymers [15, 79]. Klysov [47] defined WPCs as products made from plastic filled with cellulose fibres and other ingredients. However, the term WPC covers an extremely wide range of composite materials using plastics ranging from polypropylene to PVC and various natural fillers ranging from wood flour to flax Tangram [91]. The polymer matrix forms the continuous phase surrounding the fibrous enforcement component [70]. With phenomenal growth of wood–thermoplastic materials in the United States in recent years, they are now most often simply referred to as WPCs with the common understanding that the plastic always refers to a thermoplastic [79] and the filler can consist of various natural fibres.

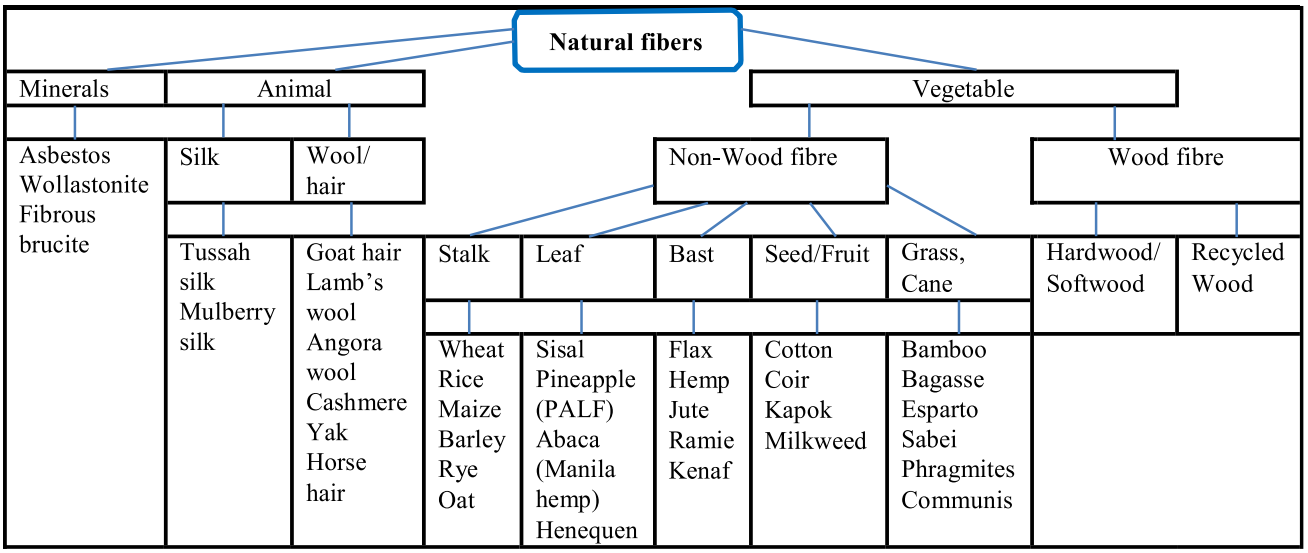
Natural fibres are fibrous plant materials produced as a result of photosynthesis. They are sometimes referred to as vegetable, biomass, photomass, phytomass, lignocellulosic fibres, agromass, solarmass, agro-based resources or photosynthetic fibres [35, 74]. The use of natural fibres dates back to about 8000 BC, specifically, the use of flax, or hemp fibre dates back to the stone age, grass and straws have been used for many generations as a reinforcement in mud bricks, whilst cotton fibres have been found in caves in Mexico that date back over 700 years [16, 35, 74, 80]. Natural fibres lost much of their interest later on, after decades of development of artificial fibres based on carbon, aramid or glass. More recently, the use of natural fibre-reinforced polymer composites has been growing again owing to their good performance, significant processing advantages, bio-degradability, low cost and low density. Natural fibre-reinforced composites with thermoplastic matrices have successfully proven their high quality in various fields of technical application [33].

Fibres like flax, hemp, coconut or jute are harvested from renewable resources, are cheap, have better stiffness per unit weight than the traditional glass and carbon fibres and have a lower impact on the environment. The advantages of natural fibres over traditional reinforcing materials, such as glass are lower cost, lower density, high toughness and a more environmentally friendly processing [35, 99, 100].

The categorisation of natural fibres is based on their origin: lignocellulosic materials, animals or minerals. The lignocellulosic fibres, also known as cellulose-based fibres, typically originate from a huge variety of softwood or hardwood species, plant fibres, such as hemp, kenaf, curaua, coir, jute, sisal, cotton or bamboo. Animal fibres include silk and leather. The most well-known mineral fibres are glass, boron and asbestos [16, 35, 53, 99]. Clearly, the most abundant are wood fibres from trees; nonetheless other fibres are also often used [16]. An overview of the classification of natural fibres from Mohanty et al. [67] is given in Table 1. All natural fibres, whether wood or non-woody, are cellulosic in nature and therefore also hydrophilic in nature.

According to Celluwood [16], Pickering [74] and Mallick [56], some of the main shortcomings and limitations of natural fibres as reinforcement for composites are related to the lower strength properties, lower interfacial adhesion,

Table 1 Classification of natural fibres



poor resistance to moisture absorption, limited maximum processing temperature and lower durability and dimensional stability. Fibre surfaces can vary greatly, which results in varying interaction with the polymer matrix due to their natural biological variability. Regions of both low and high surface energy may exist on the same fibre. Also the surface of the fibre can be smooth or rough and fibre modifications, such as beating, may enhance surface contact area [47, 70, 84]. Other factors, which can largely affect the composite properties, are concerned with the size, geometry and dispersion of filler particles in the matrix [75].

Indeed, the performance of natural fibre-reinforced polymer composites as a structural material mainly depends on the quality of stress transfer in the interphase between fibre and polymer in the composite [68]. The interphase is the region lying between the reinforcing fibre and the polymer and as such play an important role in the performance of fibre-reinforced polymer composites [68]. The load transfer between the fibre and matrix affects the overall mechanical properties of the composite [68].

To overcome the shortcoming, various techniques have been developed to modify natural fibres. There are four methods used to treat natural fibres based on the modification process: physical, chemical, biological and nanotechnological [16, 70]. Physical modification is done in order to change the structural and topological properties of the fibre, with the aim of increasing the strength of the fibres. Typical methods involve thermo-treatment, beating, calendaring and stretching [16]. Chemical modification utilises chemical agents to modify the fibre surface or the entire fibre throughout. The modification can be classified into five methods: mercerisation, oxidation, cross linking, grafting and coupling agent treatment [16, 70]. The control of properties of natural fibre-reinforced polymer composites highly depends on the possibility of modifying the interfacial adhesion through the improvement of the fibre–matrix interactions. Polymer modification appears to be a quick, effective method to provide good interfacial adhesion, in contrast to fibre modification, which generally involves solvent-based processes [75]. Compatibilising is a surface-active method, which utilises the electrostatic nature of the two interfaces [47, 70]. Compatibilisers have the primary function of improving the homogeneity of dissimilar or incompatible materials. Lack of homogeneity can prevent the development of stress transfer and reduce the mechanical properties of the end product; therefore, the use of compatibilisers improves mechanical properties [47, 70]. Biological treatments involve the use of naturally occurring microorganisms, such as bacteria and fungi to alter the surface properties of fibres. Nanotechnology is used to immobilise nanoparticles on the surface of natural fibres through layer-by-layer deposition or the sol–gel process [16].

Reinforcements for composite materials can be in the form of fibres, particles or flakes. The size of fibres used in composite materials ranges from the micrometre to the centimetre level [11, 70].

Performance and Applications

Wood fibre/plastics composites have found many applications replacing solid wood or pure plastic materials. Several Asian countries, especially India, have continuously used natural fibres, mainly jute fibres, as reinforcement for composites and are producing natural composites for many applications such as pipes, panels and other profiles. In Japan, WPCs are applied for stairs, handrails and bathrooms. In the US building products, such as decking, cladding and window frames are very successful in the market, whereas in Europe fibre composites mainly find applications in the automotive industry [35, 74].

Cellulosic fillers/fibres have been incorporated in a wide variety of polymers, such as polypropylene, polyethylene, polystyrene, polyvinyl chloride and polyamides [74, 80].

The performance of a fibre used in WPCs depends on several factors including chemical composition, physical properties, mechanical properties, the interaction of a fibre with the composite matrix and how that fibre or fibre/matrix performs under a given set of environmental conditions [35, 47, 70]. Tensile strength is the most frequently tested property of natural fibre-reinforced composites [35] as it is a good indicator for interfacial adhesion and general performance of the WPC. Rowell et al. [18, 47, 81] and others investigated the effect of coupling agents and different matrices, and Jacoby et al. [37] and Caraschi and Leao [14] studied different chemical treatments for wood fibre composites and all these were found to improve tensile properties. Pracella et al. [75] examined the effect of chemical modification of fibres, as well as the addition of compatibilisers containing reactive groups on the morphological, thermal and mechanical properties of polypropylene (PP), polystyrene (PS) and ethylene–vinyl acetate (EVA) copolymer composites containing hemp, cellulose and oat. They observed enhanced fibre dispersion and interfacial adhesion with the occurrence of effective interactions between the functional groups on the copolymer chains and the polar groups of the fibres.

Mishra et al. [66], Rout et al. [78], Cyras et al. [21], Marcovich et al. [57] and Khan et al. [42] investigated the tensile properties of composites containing jute, sisal, coir, pineapple or leaf fibre and all reported increases in the tensile, flexural and impact strength of their composites.

McDowell et al. [61], Aramguren et al. [2], Van de Velde and Kiekens [92], Chen-Jui [19], Van Den Oever [93], Heuer [34] and Rozman [82] studied the flexural properties of wood, flax, jute, coir and oil palm fibres with regard to their effect on the moulding properties, chemical treatment, esterification, different wood species, fibre loading and surface wettability. All studies agree that mechanical performance of WPCs improves significantly when compatibilisers are used under optimised conditions [70]. Dittenber and GangaRao [24] conducted a critical review of recent publications on the use of natural fibre composites in infrastructure and emphasised that using natural materials and modern construction techniques reduces construction waste and increases energy efficiency, whilst promoting the concept of sustainability. Azwa et al. [4] published a review on the degradability of polymeric composites based on natural fibres by evaluating the characteristics of several natural fibre composites exposed to moisture, thermal, fire, and ultraviolet degradation and concluded that an optimum blend ratio of chemical additives must be employed to achieve a balance between strength and durability requirements for natural fibre composites.

In their study, Le Duigou et al. [49] evaluated the fibre surface involved in the practical adhesion of flax/epoxy system by microbond and could not explain the superficial surface chemistry evaluated by X-ray photo-electron spectroscopy (XPS). Nonetheless, they established with the FTIR that the effective surface or complex interphase is the overall area where fibre and resin are in contact. Morphology and mechanical properties of wood flour-reinforced polypropylene composites were studied by Bhandari et al. [8] and their results showed that alkali-treated wood flour was more compatible with PP matrix than a neat one and the effects were reflected in the morphological and mechanical properties of the composites. They also observed that the compatibiliser played a key role in enhancing the filler–matrix interfacial interactions.

The Atomic Force Microscope

In 1982, the scanning tunnelling microscope (STM) was developed as a tool to image metallic and semiconducting surfaces with high resolution [1, 9, 51, 55, 88]. This discovery later prompted the development of several advanced high-resolution imaging techniques, which scan point probes in a raster pattern across the sample surface to detect various interaction forces. The limitation of the STM to conducting surfaces led to the development of the atomic force microscope (AFM) by Gerd Binnig, Christopher Gerber and Calvin Quate at Stanford University, USA [1, 10, 26, 55, 88]. Since then, the AFM has developed into the most widespread and commercially successful scanning probe microscope. It is used not only in physical, chemical, biological, medical and material research laboratories, but also for product development and quality control. The success of the AFM is attributed to the high resolution and the versatility, with which it can map not only the topography of sample surfaces in the sub-micrometre scale, but also physical properties depending on the interaction forces between the tip and the sample surface [26, 32, 51, 55, 65]. As elaborated by Starostina and West [88] and Prater et al. [76], the AFM is capable of producing 3D topographical information from the Å to the 1m level with high resolution. The AFM is, however, not limited to topographic images; it can also be used to identify and discriminate surfaces with varying chemical properties, for example, by modifying the AFM tip with self-assembled monolayers (SAMs) of specific functional groups [60]. The method of scanning surfaces with modified AFM probes is called chemical force microscopy (CFM) [60, 71]. Chemical force microscopy detects the chemical interaction between the functionalised tip and the surface and maps it as a 3D image, similar to the image of surface morphology and often both images can be acquired simultaneously [1, 32, 55, 76].

The AFM requires no special sample preparation and is adaptable to many different environments such as air, vacuum or liquid, as well as to a large variety of samples. The only limitation with regard to sample size is that it must be securely fixated and not too rough [1, 32, 55].

The raster pattern to create a point matrix interaction values for imaging is obtained by piezoelectric elements, which create mechanical movement to accurately move the AFM probe independently in x and y direction. The forces acting on the cantilever are measured via a laser beam that is reflected off the cantilever into a photodiode and any change in its position is counteracted by feedback control system that maintains the desired force between the probe and the sample by moving a piezo element in z direction[1, 26, 32, 55]. The force detected between the probe and the surface can be as small as 1 nN [60, 88]. Recently, an AFM-based technique where forces up to 1 mN can be applied to fibre samples has been proposed by Schmied et al. [83].

Operation Principles of the AFM

The AFM detects forces acting between a sample surface and a sharp tip which is suspended on a very soft spring called cantilever. A feedback system which controls the vertical z-position of the tip on the sample surface keeps the deflection of the cantilever constant [26, 40, 76]. To create an image, the tip is brought into close contact with the sample and raster-scanned over the surface, causing the

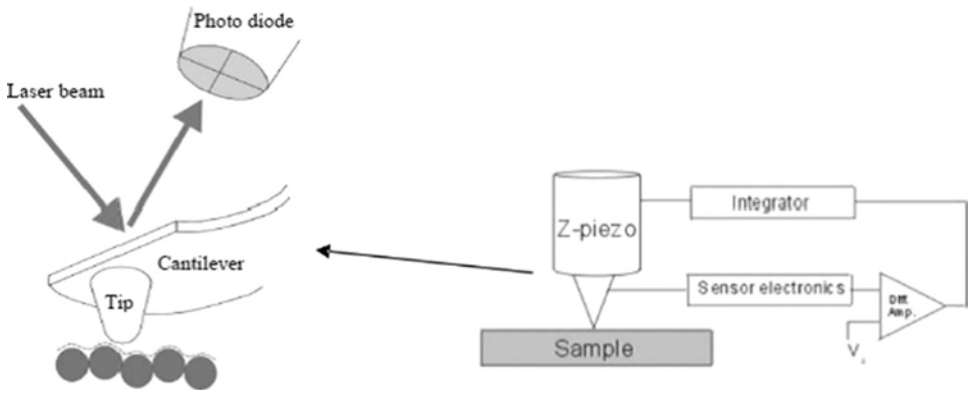


Fig. 1 Schematic diagram of the AFM

cantilever to deflect because of a change in surface topography or other interaction forces. The cantilever deflection is detected via a laser beam that is deflected off the cantilever's back side into a position-sensitive photo-diode detector [1, 51, 55, 76, 88] as shown in Fig. 1. The obtained three-dimensional data represents a 3D image of the surface topography. In non-contact mode, this information is mostly obtained from the change in VDW forces between the tip and the sample [26, 51]. Force spectroscopy on a single point on the sample can be used to provide a quantitative measure of the interaction force [64]. In this mode, the interaction force between the tip and the sample in one point is measured by analysing cantilever deflection when the probe is moved towards and away from the substrate. This deflection of the tip occurs on a straight line normal to the surface. As the tip comes in close proximity to the surface, an attractive or repulsive force causes the cantilever to deflect. If the force is attractive, the cantilever will be pulled down towards the substrate and if it is repulsive, the cantilever is pushed up. The deflection signal can be converted into the actual force value if the spring constant of the cantilever is known [1, 32, 51, 55].

The result of an AFM image is a force map, which is obtained by tracking the laser displacement between the tip and the sample (z). A force–distance (F/D) curve is obtained in the spectroscopy mode to assess the physical and mechanical properties of the sample. In a F/D curve, the approach and retraction curves are obtained for a point on the sample and a force image can be obtained by acquiring several F/D curves at different points in the x–y plane. Different parts of the F/D curve contain different information of the sample, such as surface hardness or adhesion between tip and sample and all this can be represented in different images. The information of F/D curves becomes clearer when a modified tip is used to investigate specific interactions.

Figure 2 gives an overview of the different AFM modes.

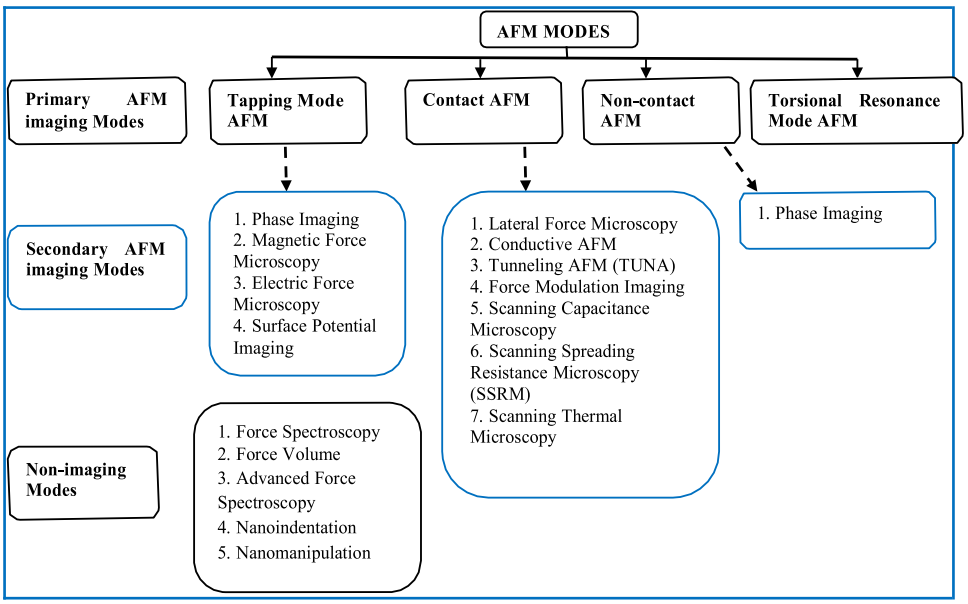


Fig. 2 AFM operation modes [95]

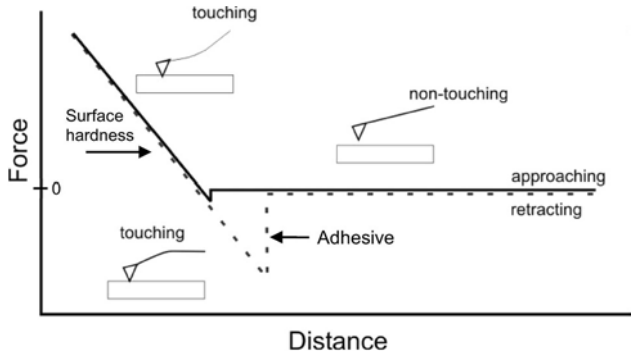


Fig. 3 Schematic force–distance relationship of cantilever deflection and vertical distance

Force Spectroscopy

Force spectroscopy is used to determine the interaction between the probe and the sample with nN resolution and provides valuable information on molecular scale with regard to the adhesion force between tip and sample [51, 60, 76].

In this mode, the cantilever is pushed into the sample at a certain point and subsequently retracted and the deflection of the cantilever is monitored as it moves towards and away from the surface resulting in a F/D curve, as shown in Fig. 3. The *x*-axis is the vertical distance between tip and sample. The *y*-axis shows the cantilever deflection as the tip is moved towards the sample surface. The F/D curve provides useful information about both long- and short-range forces as well as surface hardness [51, 76]. As the tip begins to approach the sample surface, there is no deflection. The initial contact between the tip and the surface is mediated by attractive van der Waals forces, which leads to a small negative deflection of the tip towards the surface. As the tip is further indented into the sample, the cantilever deflection increases and this part of the curve is a measure of the surface hardness, which is proportional to the gradient of the deflection. As the cantilever is retracted again, various adhesive forces between the sample and the tip maintain contact between tip and sample. These adhesive forces can be directly measured from the F/D curve. Eventually, the tip loses contact to the surface upon overcoming the adhesive forces and the cantilever is free and no deflection is measured. Forces acting between the tip and the sample surface can therefore be measured localised with nm resolution by obtaining F/D curves [32, 51, 64, 76, 85].

F/D curves can be obtained at several different surface points in order to generate a map of adhesion forces. This can be advanced by functionalising end of the tip with specific molecules to measure the specific binding strength between molecules [60] which results in an image of the distribution of functional chemical groups [51].

Many studies have made use of AFM from the biological sciences to material sciences. In his review on the application of AFM, Wallace [96] indicated that approximately 150 articles addressed the application of AFM-based techniques to investigate bone, dentin, tendon and other collagen-based tissues. In their study on the application of AFM to the characterisation of industrial polymer materials, Bar and Meyers [6] concluded that the AFM has been an enabling technology for understanding the structure and property relationships in polymeric materials including homopolymers, blends, impact-modified polymer systems, porous polymer systems and semi-crystalline polymers. Burnham and Colton [12] and DiNardo [23] demonstrated the use of the AFM as a nanoindenter and to measure surface forces on surfaces, whilst Ganser et al. [29] recently investigated the hardness and modulus of elasticity of cellulose fibres with AFM nanoindentation.

Yan and Li [97] used chemically modified –OH-functionalized AFM tips to evaluate the inter-fibre bonding properties of typical wood pulp fibres. The pull-off forces and adhesion forces were measured in aqueous media and they showed that van der Waals forces are the major contributing factor to adhesion on non-swollen solid regions of fibre surfaces.

In demonstrating the increasing number of AFM capabilities useful in studies of polymer materials, Magonov and Heaton [54] stated that the application of AFM goes far beyond high-resolution profiling by providing local properties, maps of sample composition and the ability to examine underlying surface layers.

Meincken and Sanderson [64] confirmed the advantages and capabilities of the AFM in polymer science over other analytical techniques like scanning electron microscopy, differential scanning calorimetry and the dynamic mechanical analysis with regard to the sample preparation and environment of study. To further demonstrate the versatility of the AFM, Meincken [62] determined the surface roughness and surface polarity of fibres, parenchyma cells and vessel elements of four hardwoods commonly used for pulping and observed a clear distinction between the cell types and species for the surface roughness and polarity. Frybort et al. [28] recently utilised the AFM to study the adhesion force between AFM tips and freshly cut wood surfaces. They found clear differences in polarity between freshly cut cell walls and inner cell surfaces at the microstructural level. Similarly, the surface polarity of wood fibres was determined after pretreatments and bisulphite pulping by Meincken and Matyumza [63]. They observed differences in polarity between the various wood species using the AFM in pulsed-force mode. George et al. [30] recently demonstrated how the AFM can be used as a tool to estimate the surface forces and roughness of modified fibres. They also

concluded that enzymatic and chemical methods can be used to improve the surface properties of natural fibres for composite applications. AFM in combination with image analysis was used to study the ultrastructure of transverse fibre cross sections and also identify the existence of pores across the fibre wall by Fahlen and Salmen [27]. In a related study and for the first time Keplinger et al. [41] used the scanning near-field optical microscopy (SNOM) on secondary plant cell walls of spruce, beech and bamboo and found their segmented circumferential nanostructure pattern to be consistent among various plant species. They also indicated that the limiting factor of conducting in-depth analysis with high-resolution characterisation techniques like AFM and TEM is that they provide structural but hardly chemical information, whilst chemical characterisation with FTIR and Raman spectroscopy also leads to disassembly of components or does not reach the required nanoscale resolution [41].

Interaction Forces and Interfaces

Chemical and physical interactions play an important role in many applications with the increasing use of nanotechnology. The force acting between two surfaces through an intervening medium is called surface force [13, 36, 101]. The characterisation of interfaces can give relevant information on interactions between fibre and matrix in WPCs. Jose et al. [39] identified four methods available for interface characterisation:

(1) Micro-mechanical techniques, such as fibre pull-out, micro-debonding, or micro-indentation and fibre fragmentation.
(2) Spectroscopic techniques, such as chemical analysis/ X-ray photo-electron spectroscopy, mass spectroscopy, X-ray diffraction studies, electron-induced vibration spectroscopy and photoacoustic spectroscopy.
(3) Microscopic techniques using optical microscopy, scanning electron microscopy, transmission electron microscopy and atomic force microscopy.
(4) Thermodynamic methods, which include wettability, inverse gas chromatography and zeta potential measurements.

When using the AFM to measure interfacial forces, knowledge of the interaction between the tip and the sample is critical to interpret any data correctly [55]. According to Amelinckx et al. [1], on atomic and molecular scale the electromagnetic interaction dominates over other interaction types. Nonetheless, the electromagnetic interaction gives rise to a variety of different forces which not only complicate the AFM image interpretation, but also give the potential of measuring many different physicals properties [55]. In relation to the physics and chemistry of the interacting surfaces, the adhesion property of surfaces is a consequence of interatomic and intermolecular surface forces such as van der Waals forces, electrostatic forces, chemical forces, capillary forces and others [101]. Gnanou and Fontanille [31] stated that three interaction types are responsible for the cohesion in polymers: van der Waals interactions (Keesom forces, Debye forces and London forces), hydrogen bonds and ionic bonds. In polymer composites the interaction between the polymer and the filler is developed during processing in the melt state and is a combination of van der Waals (VDW) interactions, specific chemical interactions and chemical bonds between the polymer and the filler surface [25]. In their study, Chau et al. [17] stated that the adhesion force between two surfaces physically originates from van der Waals forces, electrostatic forces, intermolecular forces, Casimir forces or meniscus forces depending on physical and/or chemical properties of those surfaces. Wallace [96] reports that a combination of interactive forces including magnetic, electrostatic and capillary forces is important in AFM depending on the separation distance; however, van der Waals forces usually dominate at small distances.

Persson et al. [73] studied the effect of capillary adhesion between cellulose fibres and found that plastic flow must occur in order to maintain good contact in the dry state.

Amelinckx et al. [1] stated that the most important forces in conventional AFM are Pauli repulsion and ionic repulsion. Three issues are of particular importance for any interaction: the strength of the force, the distance over which it acts and the environment through which it acts. Magonov and Whangbo [55] established that adhesion between two macroscopic bodies is a consequence of the long- and short-range force interactions, involving VDW forces, electrostatic force, capillary force and frictional force. Some of the long-range forces between tip and surfaces include the VDW attraction, capillary force due to the presence of fluid films at the surface when imaging in liquid or air, and electrostatic forces [13]. Table 2 gives an overview of all forces encountered in AFM, depending on the tip/sample distance as it is observed in force spectroscopy mode.

The AFM has become one of the most advanced methods for the investigation of polymer surfaces and composites in recent years due to its developmental and instrumentation successes and the invaluable information it provides on morphology, nanoscale structure and chain order of polymers [8, 40]. Consideration of the hydrophobic attraction and hydrophilic repulsion is necessary in the AFM analysis of polymer samples [8, 40, 76]. In polymers, the structure and morphology of the topmost surface layers always differ from those of the bulk

Table 2 Interactions occurring in AFM force spectroscopy (JPK Instruments)

	Interaction
Approach	
Tip far away (10–100 1m)	No interaction
Tip approaching (few 1m)	Electrostatic forces
	Long-range interactions from adsorbed molecules
Tip close to surface (several nm to A°)	van der Waals
	Capillary forces (in air)
	Double-layer forces/screened electrostatics
	Chemical potential
	Magnetic
	Solvation forces (water layering)
Contact	
Tip indenting sample	Stiffness (Young's modulus, elastic response)
	Surface hardness
	Viscoelastic response
	Measurement of active forces (e.g., generated by cells)
Retract	
Tip lifting off surface (few A°to nm)	Adhesion:
	Non-specific (including chemical affinity, surface coatings)
	Ligand-receptor
	DNA hybridisation
	Cell surface interactions
Tip further away (nm to hundreds of nm)	Stretched molecules between tip and surface: Protein unfolding, pulling out of membranes Entropic elasticity
	Structural transitions and ''melting''
	Other conformational changes in stretched molecules
Tip far from surface (1–5 1m)	Connections broken between the tip and surface, no further interactions

polymer, whilst the surface also influences properties such as adhesion, friction, wetting, swelling, penetrability and compatibility [8, 40].

Adhesion and Surface Energy

Adhesion and the interphase play a very important role in determining composite properties such as strength, toughness, creep and moisture stability [70]. Adhesion refers to the tendency of two different bodies to be held together, whilst the mechanical force that is needed to separate both bodies from another is the adhesion force or pull-off force. In theory, the work of adhesion upon separation of the surfaces is defined by the surface energy and interfacial surface tensions of the interacting materials. Adhesion allows stress transfer between two bodies and is quantified by the amount of work required to pull the two surfaces apart [70]. Differences in surface tension or free surface energy of different substances are a result of different interatomic forces. These intermolecular forces could be ionic, dipole–dipole, ion–dipole interactions, induced dipolar forces, VDW interactions, hydration forces, steric and fluctuation forces [36].

Adhesion is very relevant to many scientific and technological areas and as such has become a very important field of study in recent years [77]. There are a number of theories on how adhesion works [36]. Practically, the adhesion phenomenon observed by AFM results from two fundamental features: the surface properties (roughness, chemical heterogeneity, adsorption layer) of the materials in contact and the interaction forces between the two surfaces. These forces depend strongly on the interaction medium (air, water, vacuum) and the four fundamental contributions due to VDW forces, capillary forces, electrostatic forces for charged surfaces and static forces [72]. In polymer composites, the interaction between the polymer and the filler is developed during processing in the melt state and is a combination of VDW interactions, specific chemical interactions and chemical bonds between the polymer and the filler surface [25]. In general, the adhesion force between an AFM tip and a sample surface

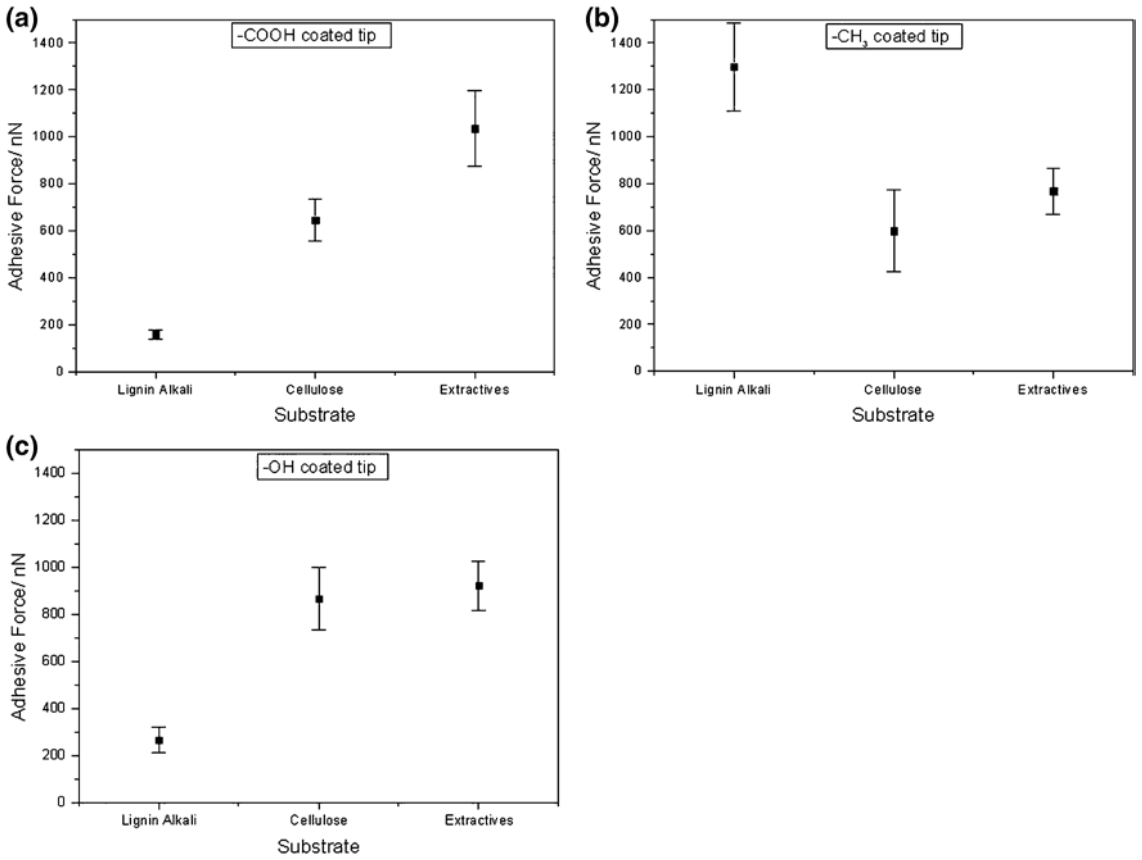


Fig. 4 Adhesive forces determined between the different substrates and a –COOH-, b $–CH_3$- and c –OH-coated tips [45]

should include the capillary force, as well as the solid–solid interactions consisting of VDW forces, electrostatic forces and the chemical bonding forces.

In AFM pull-off measurements, continuum contact mechanics models are commonly used to describe the probe/substrate system [85]. The JKR and DMT models developed by Johnson et al. [38] and Derjaguin et al. [22], respectively, are frequently used to interpret the pull-off forces measured by the AFM. The difference between the two models lies in the nature of forces assumed to beacting between particle and substrate [36]. The JKR model assumes that attractive forces act only inside the particle–substrate contact area, whereas the DMT model includes long-range surface forces operating outside the particle–substrate contact area. Both models describe the correlation between pull-off force (F) and work of adhesion (W_A) through a simple analytical equation of the following form:

$$F = c\,\pi\,RW_A, \tag{1}$$

where R is the radius of the particle (probing tip), and c is a constant (where $c = 2$ in the DMT model and $c = 1.5$ in the JKR model).

The DMT model is more appropriate for systems with hard materials having low surface energy and small radii of probe curvature. The JKR model applies better to softer materials with higher surface energy and larger probes.

To quantify adhesion energies from AFM measurements, the JKR model is frequently used for the analysis of data obtained by force–distance spectroscopy [44]. In the JKR model, the adhesion force (AFM pull-off force) is related to the work of adhesion, W_{adh}, and the reduced radius, R, of the tip-surface contact:

$$F_{adh} = -3/2(\pi\,RW_{adh}). \tag{2}$$

The work of adhesion is a combination of the tip-surface (γ_{ts}), tip-solvent (γ_l) and surface-solvent (γ_{sl}) interfacial energies ($W_{adh} = \gamma_{ts} + \gamma_l - \gamma_{sl}$). For tip-surface combinations that have the same chemical composition, the surface energy may be estimated directly from the adhesion measurement as W_{adh}.

One can, however, also directly and quantitatively determine the adhesive force from the calibration of the cantilever deflection. The deflection of the cantilever spring is directly proportional to the tip-sample interaction

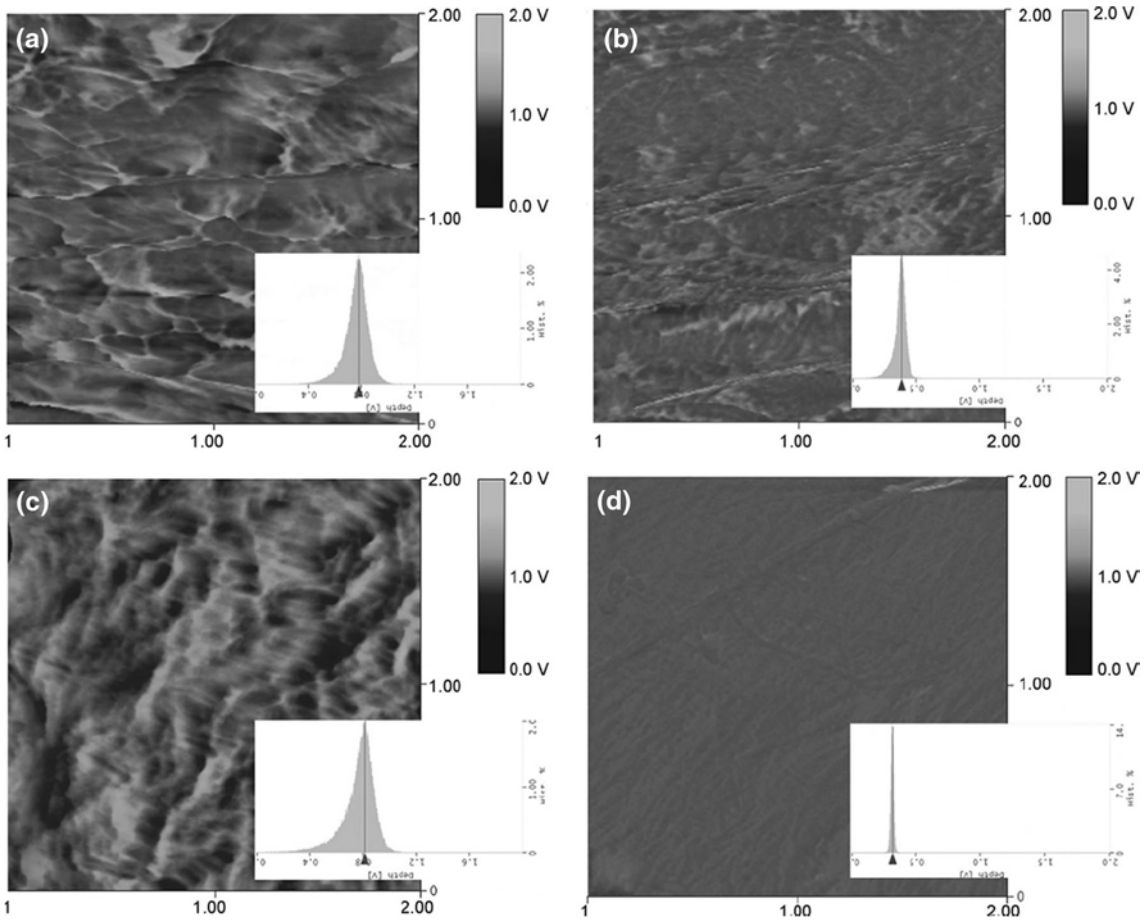


Fig. 5 Adhesive force images and histograms of *grey* values obtained on the fibre surface of pulped *E. grandis* with a –COOH- and b–CH_3-coated tips and on the fibre surface of pulped *A. mearnsii* with c –COOH- and d –CH_3-coated tips, showing the removal of lignin on the fibre surfaces [45]

force, and once the deflection of the cantilever is known as a distance x, the adhesive force F can be calculated with Hooke's law:

$$F = kx, \quad (3)$$

where k is the spring constant of the cantilever.

The spring constant of the cantilever depends strongly on its shape and material. Typical silicon or silicon nitride contact cantilevers have low spring constants of about 1.5 N/m and shorter non-contact cantilevers have spring constants in the range of 50 N/m.

Localisation and Quantification of Functional Groups

As mentioned above, the incompatibility between cellulosic fibres and polymer matrices requires the introduction of compatibilisers in WPCs. The AFM has in that respect recently opened remarkable opportunities, because it allows not only the imaging of a surface on molecular scale, but through the measurement of F/D curves allows the determination of adhesive force measurements on any given point in this image.

Klash et al. [45] studied the distribution of different free chemical functional groups on wood and pulp fibres by means of CFM with chemically modified tips, which showed different sensitivities towards the major functional groups present in the different wood components. The cellulose and lignin content on fibre surface was thus not only localised, but could also be quantified [46]. Yan and Li [97] also used AFM with chemically modified tips to evaluate the inter-fibre bonding properties of typical wood pulp fibres. In a related study, Vancso et al. [94] reviewed the recent developments in the field of high-resolution lateral mapping of the surface chemical composition of polymers by AFM and other complementary imaging techniques to unravel the lateral distribution of chemical surface groups, the stability of various types of functional groups in various environments and the interactions with controlled functional groups at the tip surface.

Figure 4 shows the quantified adhesive forces detected in air between different functionalized tips and different wood components [45].

Carboxyl (COOH) and hydroxyl (OH) groups are polar and are attracted to the polar hydroxyl groups on the cellulose surface. Lignin, on the other hand, has many non-polar functional groups that will experience higher adhesion to non-polar methyl (CH_3) groups.

The resulting AFM images then show the predominant distribution of cellulose and lignin on the wood fibre surface and can also be used to show the removal of lignin after pulping, as displayed in Fig. 5.

This information can be used to analyse differences in surface morphology of wood fibres originating from different wood species and more importantly detect possible binding sites for the compatibilisers on the wood particles. The polar ends of the compatibilisers would bind to the polar functional groups on the wood fibres, as highlighted, for example, in the image obtained with a –COOH-coated tip. From AFM measurements, it is possible to determine the distribution of binding sites, as well as the strength of the adhesive force that will hold the compatibiliser and wood fibre together. The same analysis can of course be performed in order to determine the interaction between the non-polar end of the compatibilisers and the polymer matrix. Understanding of the interaction of the WPC components on molecular scale will allow for a better understanding of macroscopic properties, such as wood fibre dispersion and general strength properties.

Conclusion

Over the last few years, WPCs have received considerable attention from the wood and plastic industries [5, 20, 86]. There are a number of advantages that natural fibres can offer compared to synthetic materials, such as sustainability, bio-degradability and environmental friendliness and reduced weight compared to synthetic reinforcement fibres. The combination of good mechanical and physical properties together with their environmentally friendly character led to an increased use of natural fibres for composite reinforcement. Nevertheless, there are also many shortcomings, specifically lower strength properties, lower interfacial adhesion, poor resistance to moisture absorption, limited maximum processing temperature and lower durability and dimensional stability. These drawbacks can be overcome by adding compatibilisers such as maleated ethylene or maleated propylene, which possess polar and non-polar functional groups that allow them to attach to the polar wood fibre surface, as well as to the non-polar polymer matrix surface. The ability of AFM to create 3D, high-resolution images of surface morphology, as well as interaction forces, has made it an essential tool for material characterisation in general. Specifically, for WPCs this technique can potentially be very useful, as they typically consist of three different components and their mechanical properties depend strongly on the interfacial adhesion between all three of them. AFM can be used to characterise the surface structure, as well as chemical functionalities of the main components and localise and to a degree quantify functional groups and therefore give an indication of the adhesive forces on a molecular scale. Other techniques, such as contact angle measurements that are typically used to determine polarity yield average values that characterise wide macroscopic areas. The high resolution of AFM allows localised measurements that take heterogeneous fibre into account and can potentially explain why certain components work in some cases better than others. For example, not all compatibilisers work equally well on all wood fibres and studying the interfacial adhesion between different compatibilisers and different wood fibres with AFM can help understand this phenomenon.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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Chapter Four

Localisation and quantification of potential binding sites for compatibilisers on soft- and hardwood in wood plastic composite systems

Summary

Understanding the adhesion properties of WPCs requires understanding of the wood and polymer characteristics and the interaction between the two components. Generally, WPCs consists of a polymer matrix, wood fillers and a compatibiliser that is able to bind to both the polar wood and the non-polar polymer by making use of specific functional groups. Therefore, for this part of the study, the tip-surface interaction forces between two different wood species and AFM tips modified with different compatibilisers were mapped to highlight the varying compatibility between the components, as well as to help determine if wood species invasive to South Africa can be used to manufacture WPCs with commercially proven compatibilisers.

Wood surfaces, namely pine and beefwood were analysed with compatibiliser modified tips to detect potential binding sites for the compatibiliser on the wood surface. The investigated compatibilisers were the commercially often used poly(ethylene-vinyl-co- alcohol) (EVOH) and poly(ethylene-graft-maleic anhydride) (PE-g-MA). Microtomed wood sections of the wood were used for analysis. All measurements were performed on an Easy Scan 2 AFM, in the advanced spectroscopy mode using force modulation cantilevers. Topography images were acquired in a 2 × 2 μm scan area with a 256 pixel resolution. To acquire the force maps, a 20 x 20 grid with evenly spaced points was defined in a roughly 2 × 2 μm scan area on the topography image and on each point a force distance was obtained. The resulting force map was created with SPIP imaging software.

It was observed that the interaction forces between the EVOH coated tip and the wood

surface were highly species sensitive, whereas adhesive forces measured between the PE-g-MA coated tip and the wood surface were comparable for both wood species. The force maps showed that wood species differ in the distribution of functional groups and the force histograms showed that the frequency distribution of the adhesive forces varied for the two wood species. The adhesive force maps clearly showed a difference between wood/compatibiliser systems, which can be related to the chemical composition of the wood species. The results confirmed that not all compatibilisers are equally suitable for all wood species and this was confirmed by mechanical tensile tests of WPC systems in another study. The study demonstrated that it is possible to map the spatial distribution of chemically distinct functional groups on the cell wall surface of wood when functionalised compatibiliser tips are used, which gives a good understanding of the adhesion mechanism between the cellulosic fibers and compatibilisers to help predict the strength properties of WPCs.

Researcharticle

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Localisation and quantification of potential binding sites for compatibilisers on soft- and hardwood in wood–plastic composite systems

Bernard Effah,[a] Albert van Reenen[b] and Martina Meincken[a]*

Chemical force microscopy (CFM) was used to characterise the surface of pine and beefwood with atomic force microscopy (AFM) tips coated with different compatibilisers. With the resulting force images, potential binding sites for compatibilisers, used in wood–plastic composites (WPC) to enhance adhesion between two relatively incompatible phases, were localised and quantified. Tips were coated with two commercially available polymers namely ethylene vinyl alcohol (EVOH) and polyethylene-grafted maleic anhydride(PE-g-MA). It could be observed that the interaction forces between the EVOH coated tip and the wood surface was highly species sensitive, whereas adhesive forces measured between the PE-g-MA coated tip and the wood surface were com- parable for both wood species. The force maps show that wood species differ in the distribution of functional groups, and the force histograms show that the frequency distribution of the adhesive forces varied for the two wood species. The adhesive force maps clearly show a difference between wood/compatibiliser systems, and the differences can be related to the chemical composition of the wood species. The results confirm that not all compatibilisers are equally suitable for all wood species and these results were confirmed by mechanical tensile tests of WPC systems in a related study.

Keywords: adhesive force; chemical force microscopy; compatibilisers; force mapping; wood surfaces; wood–plastic composites

Introduction

In recent years, atomic force microscopy (AFM) has become a technique of choice for non-destructive surface imaging of various materials and characterisation with a molecular or even atomic resolution. AFM is commonly used for the measurement of long- and short-range surface forces from microscopic scale down to molecular level.[1] The success of the AFM is attributed to the high resolution and the versatility, with which it can map not only the topography of sample surfaces, but also physical properties de- pending on the interaction forces between the tip and the sample surface.[2,3] Prior to the birth of the scanning tunnelling microscope (STM) and subsequently the AFM, researchers mainly relied on optical and electron microscopy for imaging and measuring the microstructure and morphology of samples.[4] Since then, the AFM has developed into a widely used technique to study the microscopic properties of surfaces and interfaces.[5]

AFM can also be used to identify and discriminate surfaces with different chemical properties by modifying the tip with self-assembled monolayers (SAMs) of specific functional groups.[6] This method of scanning surfaces with modified probes is called chemical force microscopy (CFM),[7] which allows to analyse functional chemical groups on the sample surface and their interactions with the tip on a scale of nN under a variety of environmental conditions.[4,8–10] In CFM, the chemical interaction between the functionalised tip and the surface is mapped resulting in a 3D image, similar to the topography image obtained by measuring van der Waals forces between the tip and sample, and often both images can be acquired simultaneously.[11,12]

When AFM is used to determine forces from force–distance curves, it typically provides information of the interaction force of one point on the sample surface at a time. However, the force volume technique makes it possible to obtain force curves at several scan points throughout an image and compose them to display a map of the chemical interaction forces across a sample.[13] With the recent development of various advanced surface characterisation techniques, the understanding of material surfaces has significantly improved making it possible to control and tailor surface characteristics for specific applications on a molecular scale. CFM can be employed to examine surface topography and functionality at high resolution and confirm if the surfaces meet the requirements. CFM allows the analysis of chemical interactions quantitatively as well as qualitatively, measuring adhesive forces between different materials on a molecular scale, which helps to explain physical and mechanical properties of the material on a macroscopic scale.

The surface properties of wood play an important role when it is to be processed into composite materials, such as wood–plastic composites (WPC).[14,15] The surface properties of wood particles

* Correspondence to: Martina Meincken, Department of Forest and Wood Science, Stellenbosch University, Stellenbosch, South Africa.
E-mail: mmein@sun.ac.za

a Department of Forest and Wood Science, Stellenbosch University, South Africa

b Department of Chemistry and Polymer Science, Stellenbosch University, South Africa

are determined by the morphology of the cell wall and cell type at the surface of the wood particle[16] and more specifically the chemical functional groups on the surface. Understanding the adhesion properties of WPCs requires understanding of the wood and polymer characteristics and the interaction between the two components.[15] In WPCs, the efficiency of stress transfer from the polymer matrix to the wood filler is affected by the surface properties of both materials. A typical WPC consists of a polymer matrix, wood fillers and a compatibiliser that is able to bind to both the polar wood and the non-polar polymer by making use of specific functional groups. Despite the good reinforcement properties of wood fillers in WPCs, an understanding of the adhesion mechanism between cellulosic fibres and the compatibiliser, as well as between the compatibiliser and the polymer is a requisite for predicting the strength properties of WPCs.[17]

The potential of wood reinforced polymer composites for use in industrial applications significantly depends on their mechanical properties. The properties of WPCs are mainly affected by the raw materials, fibre content and in some cases processing parameters.[18] The strength of WPCs is determined by the fibre strength and by the ability of the matrix to transmit stress to the fibre, which is affected by the fibre aspect ratio, orientation, geometry and the interfacial bond between fibre and matrix.[18,19] Additionally, a successful WPC formulation depends to some extent on parameters, such as the influence of moisture, unfavourable chemical interactions of adhesive and matrix, morphology of components, stability under ambient and varying conditions and cost.[20] To achieve better mechanical properties the interfacial adhesion should be strong to ensure stable interface in WPCs.

Default commercial AFM tips are made of silicon or silicon nitride for assessing basic surface properties. This type of probe lacks chemical specificity or the ability to identify specific chemical functional groups on a surface.[8] CFM uses chemically modified tips to transform the AFM into a tool to measure specific chemical interactions, mostly by measuring adhesion and friction between tip and sample surface, as well as imaging surface topography.[10] A number of relevant studies describe the use of various functionalised AFM tips to evaluate surface properties of different materials. More specifically, on wood surfaces, Yan and Li[21] used chemically modified —OH (polar hydroxyl groups) functionalised AFM tips to evaluate the inter-fibre bonding properties of typical wood pulp fibres. The pull-off forces and adhesion forces were measured in aqueous media, and they showed that vander Waals forces are the major contributing factors to adhesion on non- swollen solid regions of fibre surfaces. Klash *et al.* [22] determined the adhesive forces between AFM tips coated with —OH (polar hydroxyl groups), —CH_3 (non-polar methyl groups) and —COOH groups. They observed that the tip coatings showed a different sensitivity towards the major chemical components present in wood fibres, namely cellulose (polar) and lignin (non-polar). Tips functionalised with -CH_3 groups were used to study the topographic effects on chemical force (adhesive force) mapping by Sato *et al.*[23], who found that the main origin of peak broadening in the histogram was caused by a topographic effect. Functionalised tips were used to discriminate chemical functionalities of a binary system of mixed self-assembled monolayers (SAMs) consisting of -CH_3 and -COOH terminating alkane thiols by Okabe *et al.*[24]. They found that the -CH_3 tips in pure water clearly discriminated the hydrophobic -CH_3 terminating domains embedded in the -COOH terminating SAM matrix.

In this study, the tip-surface interaction forces between two different wood species and AFM tips modified with different polymeric compatibilisers were mapped to highlight the varying compatibility between the components. This complements a related study, where significant differences between the wood species and compatibilisers were found on macroscopic scale[25].

The investigated wood species are species invasive to South Africa, and which are not currently used for commercial composite material production. These wood species need to be cleared from commercial land, and the development of value added products from them is one of the government priorities. The results of this study show that the wood species differ significantly in their surface characteristics and that not all compatibilisers work equally well with different wood species, which means that great care needs to be taken when wood species other than the commercially proven ones are to be incorporated in to WPCs.

Materials and methods

Sample preparation

The compatibilisers used to coat the AFM probes were the commercially available poly(ethylene-co-vinyl alcohol) (EVOH) and maleic anhydride-grafted polyethylene (PE-g-MA), both from Sigma-Aldrich. Wood was obtained from a soft- and hard wood species invasive to South Africa, namely Pine (*Pinus radiata*) and Beefwood (*Casuarina cunninghamiana*).

Clear and defect free wood samples of 20 × 20 × 20 mm^3 from pine and beefwood were prepared from stem wood. The samples were dried in a conditioning room and stored in a desiccator until microtoming. Thin slices of about 40 μm were cut in longitudinal direction (along the grain) with a Leica RM 2245 rotary microtome with a 16-cm steel blade. The sections were secured on a glass substrate with double sided adhesive tape and subsequently conditioned at 20 °C and 65% RH for 48 h before CFM analysis.

Chemical modification of AFM tips

Two general approaches exist to functionalise AFM tips: first, the direct amination of the tip by silanisation or esterification and second the amination via a thiol-based self-assembled monolayers (SAM) on a gold coated tip. The latter approach was used in this study, as the thiol groups have a high affinity to gold and thereby form strong (covalent) bonds that ensure that the tip–end-group interaction is stronger than the end-group–surface interaction. The acyl chains of the SAM form a very dense and closely packed structure, which rigidifies it and also increases the robustness of the tip functionalisation.[26] The compatibilisers were attached to the SAM surface via adsorption through dipping.[26,27] Silicon force modulation cantilevers from Nanosensors (Switzerland) were used for CFM analysis in this study. They were modified according to Bastidas *et al.*[9] and functionalised with the compatibilisers, namely EVOH and PE-g-MA. The silicon tips were first gold coated with an Edwards S150A Gold Sputter Coater and cleaned under a 254-nm UV lamp for 1 h to ensure that all organic material was re- moved. A 1 mM thiol solution of 11-mercapto-1-undecanol, 1- octadecanethiol and11-mercapto undecanoic acid (Aldrich) in ethanol (KIMIX) was prepared, into which the gold tips were submerged for 2 h at room temperature under Argon gas. The thiol- based SAM was formed via adsorption of the alkanethiol molecules to the gold coated tips by covalent bonding. A 2 mM solution of each compatibiliser was prepared in xylene (PE-g-MA) and DMSO (EVOH) at 40 °C, into which the thiol coated tips were dipped for 2 h to prepare functionalised tips with free maleic anhydride and

hydroxyl functional groups, respectively. The terminating end group molecules of EVOH and PE-g-MA compatibilisers were attached to the tip via chemical absorption through hydrogen bonds to the thiol end of the SAM layer. The coated tips were then rinsed with n-heptane (KIMIX) and alcohol, and dried in an argon stream for 48h and stored until use.

To ensure that the tips were successfully functionalised with EVOH and PE-g-MA terminated molecules, the process used by Maver *et al.*[27] was followed. Scanning electron microscope and energy dispersive x-ray analysis (EDX) were used to ensure that the functionalisation was confined to the actual end of the tip, and that the aspect ratio had not changed too much and that the desired functional groups were at the tip end.

Adhesive force determination with CFM

All measurements were performed on an Easy Scan 2 AFM from Nanosurf (Switzerland) in the advanced spectroscopy mode. Force modulation cantilevers with a 2 N/m spring constant from Nanosensors were used, and the tips were chemically modified as described in the Section on Chemical Modification of AFM Tips. Topography images were acquired with a 2×2 μm scan area with a 256 pixel resolution. The measuring area was identified in a larger (40 × 40 μm) topography image, and it was ensured that it was located on the convex outer surface of the cell. For the force mapping a 20 × 20 grid with evenly spaced points was defined in a roughly 2 × 2 μm scan area on the topography image, and on each point a force distance was obtained. The resulting force map was created with the imaging software SPIP (6.0.14 and 6.2.0). Measurements were performed in a closed environment to minimise outside effects, such as humidity or temperature changes.

Results and discussion

To understand how WPCs made with two different invasive wood species and two different compatibilisers perform, microscopic adhesive forces between wood and compatibiliser were determined. These two species differ significantly in their chemical and physical properties. Pine, a softwood with uniform, long tracheids and no large pores is similar to other softwood species, which are commonly used for WPC production, while beefwood, a hardwood and porous species differs significantly with regards to cell type and structure. Softwoods typically consist of trachieds (90%) and small parenchyma cells (10%). In contrast, hardwoods contain shorter fibres, vessel elements, parenchyma cells and ray cells, resulting in a very inhomogeneous surface.[28] The chemical composition of both soft- and hardwood is generally a complex phenomenon with large variations between and within species. Pine typically contains around 32% cellulose, 22% lignin and 6% extractives.[29] Beefwood[30] is reported to have a slightly different composition, with higher cellulose (38%) and lignin (25%) content and slightly less extractives (5%). The remaining content is mostly made up from amorphous hemi-celluloses, which provide the majority of binding sites, in the form of polar hydroxyl groups, to the compatibiliser. For pine, this is around 40% and for beef- wood around 32%. Softwoods generally have an average tracheid length of 4 mm whilst hardwoods have shorter fibres around 1 mm long.[30]

The pH, which might affect the chemical properties of the wood and therefore the performance of the WPC, was determined to be 4.78 for pine and 6.1 for beefwood. In the practical WPC production, softwoods are usually preferred over hardwoods because of their high aspect ratio and their regular cellular structure.[28]

EVOH is a copolymer composed of ethylene (44%) and vinyl alcohol (56%). The vinyl alcohol is expected to interact with the polar hydroxyl groups of the wood, whilst the hydrophobic ethylene interacts with the polymer matrix, but it may also interact with the non-polar lignin on the wood surface. PE-g-MA contains polyethylene with maleic anhydride grafted onto it. The anhydride groups are expected to interact with the hydroxyl groups of the wood surface, while the ethylene backbone reacts with the hydrophobic elements, such as the polymer matrix or lignin.

Force mapping

Force maps containing 400 force measurements were performed across the sample surface at five different positions on each sample, as indicated in Fig. 1. The square area indicates an area where the force was mapped in a 20 × 20 grid, and the arrow indicates the fibre direction.

Areas with large adhesive forces are indicated by lighter colour, whereas low adhesive forces (darker colour) represent areas where the compatibiliser does not interact well with the wood surface. Surface areas that showed strong interaction with the functionalised tip exhibited larger adhesion than those with weaker interactions; therefore, the lighter areas in the image can be regarded as potential binding sites for the compatibiliser.

Figures 2a–d show the adhesive force maps of EVOH and PE-g-MA coated tips on pine and beefwood, respectively. The arrow indicates the fibre orientation.

The EVOH coated tip clearly showed more potential binding sites on pine than on beefwood as displayed in Figs 2a and 2b, while the potential binding sites for PE-g-MA appeared more on beefwood than pine, as displayed in Figs 2c and 2d.

The adhesive force maps highlight potential binding sites between the functional groups of the compatibiliser and the cell wall surface on a molecular scale, as the resolution of the force map is about 100 nm, and clearly show a difference between the wood/compatibiliser systems. EVOH seems to be more sensitive to the wood species, which may be explained by the surface structure and chemical composition of the cell wall of the wood species. Pine, a softwood, has a less complex anatomical structure and is mostly composed of tracheids and parenchyma cells. Hardwoods have a more complex anatomy, containing fibres, vessel elements, ray and parenchyma cells in different ratios. Apart from the structural differences, the wood species differ in their chemical composition, which obviously affects the type and amount of chemical functional groups on the cell surface, to which compatibilisers can

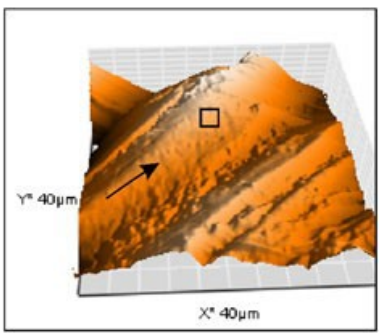

Figure 1. AFM topography image, indicating the fibre orientation and the area of force mapping.

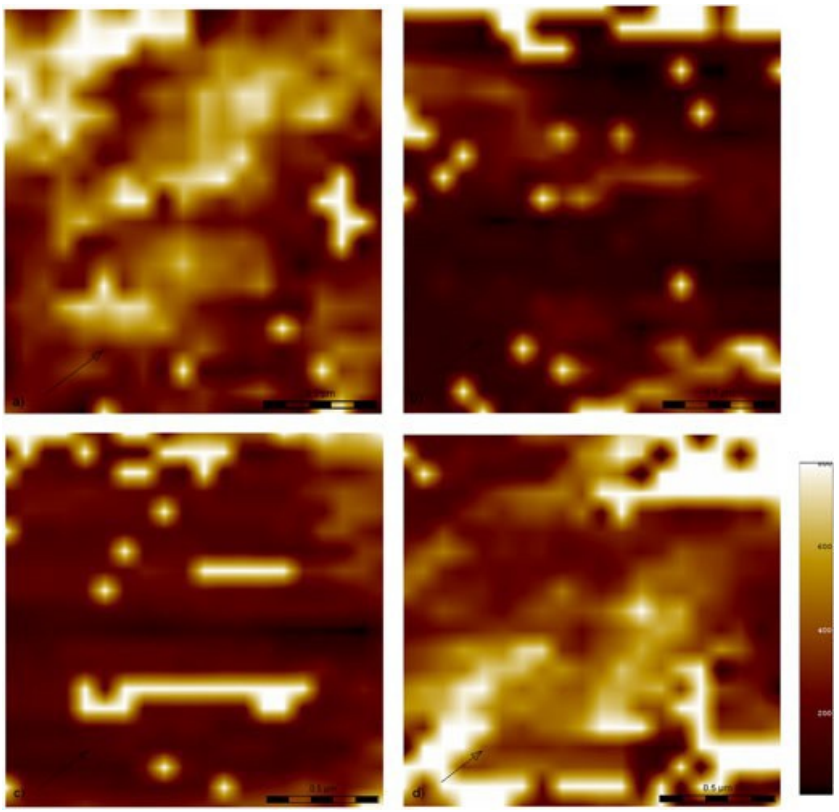

Figure 2. Adhesive force map of the EVOH coated tip on a) pine and b) beefwood and the PE-g-MA coated tip on c) pine and d) beefwood.

bind. Wood cells consist largely of cellulose, hemicelluloses and lignin with a varying amount of extractives in the cells. The polar functional groups, to which the compatibilisers bind, are mostly hydroxyl (-OH) groups of the hemicellulose, as the hydroxyl groups of cellulose are to a large extent used to bind cellulose chains to each other, resulting in the crystalline structure. As explained above, pine has a higher hemicellulose content, which results in more potential binding sites. A high lignin content, on the other hand, may impact the surface polarity of the wood particles negatively, as the functional groups of lignin are predominantly non-polar.[22]

Adhesion quantification

To quantify the interaction differences between the different wood/compatibiliser systems, the adhesive forces obtained from the force maps were represented as histograms, as shown in Fig. 3. They show the distribution of the adhesive forces determined across the scan areas. High values are correlated to potential binding sites for the compatibiliser on the wood surface. For the EVOH coated tip, more binding sites were observed on pine than on beefwood, which can clearly be seen in Fig. 3 where the frequency of high adhesive forces is much higher than on beefwood. The average adhesive forces and standard deviations obtained from the force maps obtained on pine and beefwood cell wall surfaces with EVOH and PE-g-MA coated tips are presented in Table 1.

It can be seen that the average adhesive forces between the EVOH coated tip and pine wood are with 405.5nN almost twice as high as on Beefwood (207.8 nN). On the other hand, the PE-g-MA coated tip showed a smaller average adhesive force of 288nN on pine wood and a somewhat higher average adhesive force of 324 nN on beefwood. The standard deviations are fairly high in all cases, as the distribution of force values ranges from very low to very high. Therefore, the actual distribution with its maximum and minimum values and its shape are of more interest than the average value and standard deviation.

The interaction forces between EVOH and pine ranged from 80 to 800 nN with the average of 405 ±160.5 nN, a peak width of 25 nN and a total distribution width of 725 nN. In Fig. 3a, it can be seen that the low interaction forces below 500 nN (dark colour) cover most of the wood cell wall surface, whilst areas of high interaction (light colour) were significantly less and as Fig. 2 showed fairly localised. This was significantly more pronounced on beefwood, where nearly all interaction forces were below 500nN. The average interaction force between EVOH and beefwood was 207.8 ±219.5 nN with a peak width of about 80 nN and a total distribution width of 680 nN. It can be seen from Fig. 3b that less than 5% of the values were between 400 and 700nN, causing the high deviation from the mean as the majority (71%) were weak adhesion forces below 200nN.

The adhesive forces detected between PE-g-MA and the different wood surfaces are displayed in Figs 3c and 3d. The adhesive forces detected on pine were somewhat lower than for EVOH and ranged from 20 to 700 nN, with an average of 288 ±145.7 nN, a peak width of 20 nN and a total distribution width of 620 nN. The interaction forces between PE-g-MA and beefwood covered a range from 0 to 800nN with an average of 324±113.1nN, a peak width of 20 nN and a total distribution width of 790 nN.

It could be observed that a wider peak width resulted in higher interaction between compatibiliser and wood surface, which also resulted in better mechanical strength, as published in previous work[25]. As displayed in Fig.3, the adhesive forces between EVOH and pine were normally distributed, whilst the distribution of

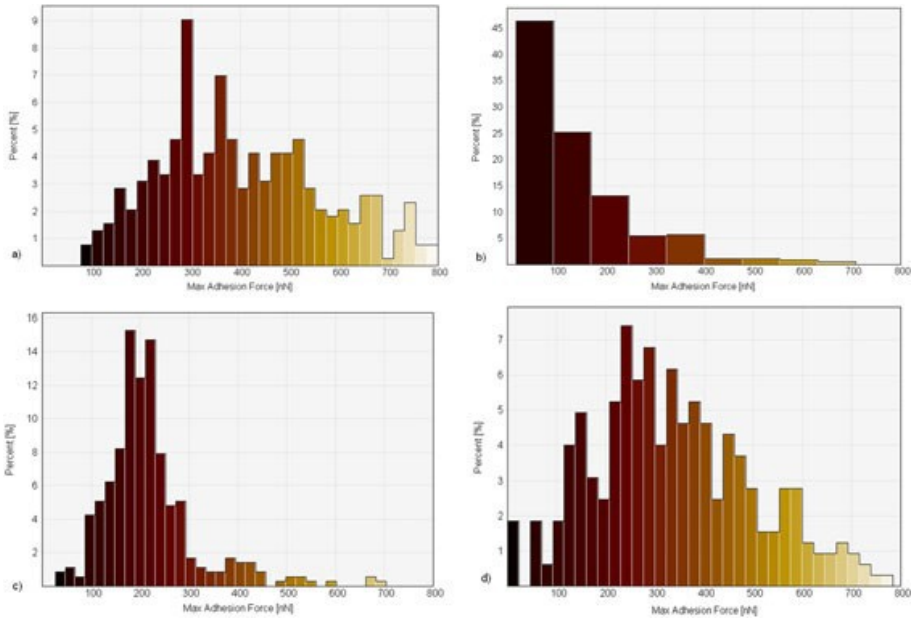

Figure 3. Frequency distribution of adhesive forces detected between EVOH and a) pine and b) beefwood and PE-g-MA and c) pine and d) beefwood.

Table 1. Average adhesion forces between compatibiliser and wood surface

Adhesion force (nN)		
Compatibiliser/species	EVOH	PE-g-MA
Pine	405.5±160.5	288±145.7
Beefwood	207.8±219.5	324±113.1

adhesive forces between EVOH and beefwood were skewed towards lower values. The opposite was observed for the distribution of adhesive forces between PE-g-MA and Pine, which was skewed towards lower values, while the distribution of adhesive forces was normal on Beefwood.

EVOH had more potential binding sites on pine than on beefwood, which means that not as many bonds would be formed between the compatibiliser and the wood surface, if this combination was used in a composite. The weaker adhesive forces may the potentially affect the tensile strength negatively in an EVOH/beefwood composite, because the weak wood/ compatibiliser interaction translates into a weak polymer/wood interaction and therefore a weak stress transfer. The distribution of the binding sites for EVOH on pine was normal, while on beef- wood it was skewed towards lower values.

PE-g-MA did not show such large species dependent differences, and the average amount of potential binding sites for PE-g-MA was comparable for both wood species. However, the distribution of adhesive force values on beefwood was normal, while it was skewed to lower values on pine.

The differences observed in the performance of the compatibilisers could be attributed to the chemical variations between the wood species, which inherently affects how they react with the compatibilisers. Additionally, the composition of the compatibilisers may have contributed to the reaction process. The maleic anhydride group of PE-g-MA reacts with the hydroxyl groups of cellulose and hemicelluloses to form an ester bond, thereby creating a covalent bond to the wood fibres. EVOH, on the other hand, is a copolymer with polar hydroxyl groups, which react with the -OH groups of the wood surface to form hydrogen bonds. In addition, the low amount of potential binding sites of EVOH on beefwood may be caused by unfavourable properties of the wood cell wall surface, such as high extractive content, or the near neutral pH value (6.1) of the wood. It is known that species with high extractive content are difficult to process into composite materials.[19]

Extractives for example can potentially affect the penetration depth of adhesives into wood. In WPCs, the polymer is supposed to penetrate enough into the wood to result in strong interaction, as the degree of penetration affects the bond quality and a proper balance needs to be obtained to avoid under- or over-penetration to prevent poor bonding.[31]

Conclusion

Understanding the surface properties of wood is crucial to understand the interaction of the components in WPCs. This study investigated the adhesive forces acting between two wood surfaces and two compatibilisers with CFM.

The aim of the study was to determine if wood species invasive to South Africa can be used to manufacture WPCs with the commercially proven compatibiliser systems.

Different wood surfaces, namely pine and beefwood were analysed with compatibiliser modified tips to detect potential binding sites of the compatibiliser on the wood surface. The investigated compatibilisers were the commercially often used EVOH and PE-g-MA.

It was observed that EVOH was very sensitive to the wood species, whereas PE-g-MA showed comparable results for both species. The force maps clearly show that the amount of binding sites for EVOH differed on the two wood species, whereas the amount of binding sites for PE-g-MA seemed fairly evenly distributed on both wood species. The force maps show that the investigated wood

species differ in the distribution of functional surface groups and that not all compatibilisers are equally suitable.

The histograms of the adhesive forces detected on the cell wall surfaces show that the distribution varied with the species and compatibiliser system used. EVOH had more potential binding sites on pine than on beefwood, indicated by the amount of high value adhesive forces. The distribution of adhesive forces relates fairly well to their macroscopic tensile strength in a related study by the authors[25]. The study demonstrates that it is possible to map the spatial distribution of chemically distinct functional groups on the cell wall surface of wood when functionalised compatibiliser tips are used.

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Chapter Five

Chemical force microscopy analysis of wood plastic composites produced from different wood species and compatibilisers

Summary

The behaviour of WPCs is best explained on the basis of the combined behaviour of the reinforcing element, the matrix and the interface. The interaction between the fiber and matrix is one of the determining factors for the formation of WPCs and their mechanical properties depend strongly on the interfacial adhesion between all three components. In this study, the adhesive forces between AFM tips coated with compatibilisers and wood cell wall surfaces were investigated. Additionally, the tensile strength of WPCs made from different wood species, low density polyethylene (LDPE) and three compatibilisers were examined. The adhesive forces determined on a molecular scale were then related to the macroscopic properties of WPCs in an attempt to explain the mechanical properties, such as tensile strength of WPCs.

Wood from six invasive tree species, namely Pine (*P. radiata*), Eucalyptus (*E. grandis*), Black wattle (*Acacia mearnsii*), Long-leaved wattle (*A. longifolia*), Port Jackson (*A. saligna*) and Beefwood (*Casuarina cunninghamiana*) was investigated and WPCs containing wood from the six species, low density polyethylene (LDPE) and three different compatibilisers, namely the commercially available Poly(ethylene- vinyl-co- alcohol) (EVOH), Poly(ethylene-graft-maleic anhydride) (PE-g-MA) and thermally degraded LDPE (dPE) were studied. The analysed properties included moisture content, density, tensile strength and adhesive forces between the wood and compatibiliser components. WPC samples were compounded and injection molded. The adhesive forces were determined using chemical force microscopy (CFM) with compatibiliser coated tips.

EVOH as compatibiliser proved to be very sensitive to the wood species incorporated into the WPC blend on both scales. Composites containing PE-g-MA and dPE as compatibiliser had a higher tensile strength for all the wood species. Composites containing dPE as compatibiliser

showed less variation in all samples for tensile strength and adhesive force. The densities and tensile strengths of the samples compared well with some commercial WPCs. The study showed that the inexpensive dPE outperforms commercially available compatibilisers and effectively promotes adhesion in WPCs. It was also shown that the studied invasive wood species can be incorporated into WPCs, if the correct compatibiliser is chosen. A positive correlation was found between microscopic adhesive force and macroscopic tensile strength, however, the results are sometimes complicated to correlate, due to the many external factors, such as the wood species, moisture content, density, compatibilisers and processing method. Nevertheless, the microscopic properties correlated well to the macroscopic properties of the WPCs.

Chemical force microscopy analysis of wood plastic composites produced from different wood species and compatibilisers

B. Effah†
PhD Student
Department of Forest and Wood Science
University of Stellenbosch, South Africa
E-mail: 18761569@sun.ac.za

K. Raatz
MSc Student
Department of Forest and Wood Science
University of Stellenbosch, South Africa
E-mail: 16228065@sun.ac.za

A. Van Reenen
Professor
Department of Chemistry and Polymer Science
University of Stellenbosch, South Africa
E-mail: ajvr@sun.ac.za

M. Meincken†*
Associate Professor
Department of Forest and Wood Science
University of Stellenbosch, South Africa
E-mail: mmein@sun.ac.za

* Corresponding author

† Society of Wood Science & Technology member

ABSTRACT

Alien invasive species (AIS) are posing a serious and direct threat to biodiversity, water security and productive use of land in South Africa. Most of these species need to be cleared and are therefore regarded as waste material, which could become raw material for wood plastic composites (WPCs). WPCs containing wood from *Pinus radiata*, *Eucalyptus grandis*, *Acacia mearnsii*, *A. longifolia*, *A. saligna* and *Casuarina cunninghamiana* trees, low density polyethylene (LDPE) and three different compatibilisers: namely the commercially available pol(ethylene-co-vinylalcohol) (EVOH), poly(ethylene graft-maleic anhydride) (PE-g-MA) and thermally degraded low density polyethylene (dPE) – were studied. The determined properties included moisture content, density, tensile strength and adhesive forces between the wood and compatibilizer components. The adhesive forces were determined using chemical force microscopy with functionalised, coated tips. WPC samples were compounded and injection molded. EVOH as compatibilizer proved to be very sensitive to the wood species incorporated into the WPC blend. Composites containing PE-g-MA and dPE as compatibilizer had a higher tensile strength for all the wood species. Composites containing dPE as compatibilizer showed less variation in all samples for tensile strength and adhesive force measurements. The densities and tensile strengths of the samples compares well with some commercial WPCs.

The study shows that the inexpensive dPE outperforms commercially available compatibilizers and effectively promotes adhesion in WPCs. It was also shown that the studied invasive wood species can be incorporated into WPCs, if the correct compatibilizer is chosen. The differences in the results of the study seem difficult to relate due to the many factors such as the wood species, moisture content, density, compatibilizers and processing method. However, the micro properties can give enough information regarding the macro properties of WPCs.

Keywords: Alien invasive species, compatibilizer, adhesive force, chemical force microscopy, tensile strength, WPCs

INTRODUCTION

Increasing environmental concerns have necessitated the search for new materials with high performance at affordable costs. Likewise, the growing dependency on petroleum-derived plastic materials and the rising environmental and sustainable concerns have motivated researchers to explore new materials to replace conventional plastic in various applications (Sarifuddin and Ismail 2015). Wood-plastic composites (WPCs) are a relatively new material class that cover a broad range of composite materials utilising an organic resin binder (matrix) and fillers composed of cellulosic material. Over the last few years, WPCs have received considerable attention from the wood and plastic industries (Balasuriya et al. 2001; Shebani et al. 2012). The properties of WPCs differ from solid wood and pure plastic in the sense that they combine the advantages of both materials, which makes it a good replacement material for some applications (Kazemi-Najafi et al. 2012). WPCs possess the further advantage that they can be made from waste products from the forestry/wood industry and recycled plastic obtained from household waste (Teuber et al. 2013).

The polymer matrix of WPCs frequently comprises polyolefins, such as low density polyethylene (LDPE) or polypropylene (PP), or polyvinyl-chloride (PVC), whereas the wood fillers are typically softwood fibers that have a well-known chemical composition and uniform configuration (Schneider 2007). Wood is an organic and natural composite of cellulose fibers embedded in a matrix of lignin and rich in functional groups with numerous hydroxyl groups. On the other hand, most matrix polymers are hydrophobic in character and have very few functional groups. This brings about chemical incompatibility, which results in poor adhesion between the two phases and also causes non-uniform dispersion of fibers within the matrix leading to poor mechanical properties (Yang et al. 2007). In order to improve the affinity and adhesion between fibers and the polymer matrix in production, chemical “coupling” or “compatibilizing” agents are typically employed (Kim et al. 2006; Stark and Rowlands 2007; Feifel et al. 2015). These compatibilizers have a polar and non-polar ends, which attach to the wood fiber and polymer, respectively. Their primary function is to improve the homogeneity of dissimilar or incompatible materials, as lack of homogeneity can reduce the mechanical properties of the end product (Niska and Sain 2008; Stokke et al. 2013). Ethylene vinyl alcohol (EVOH) and Polyethylene graft-maleic anhydride (PE-g-MA) are some of the typically used conventional compatibilizers for WPCs. The ethylene segment in EVOH is compatible with the non-polar polymeric matrix and the hydroxyl-containing component attaches to the wood

filler. Similarly, the ethylene in PE-g-MA has an affinity to the polymer matrix, while the maleic anhydride attaches to the wood surface. Thermally degraded LDPE has proven to be a good compatibilizer for WPCs (Ndlovu et al. 2013). When LDPE undergoes thermo-oxidative degradation, carbonyl and hydroxyl groups are produced and these new functional groups allow the polymer to be used as a compatibilizer for WPCs (Ndlovu et al. 2013).

In recent times, the increased use of WPCs for structural and exterior applications has resulted in the need to understand the durability of WPCs better (Stark and Matuana 2007). It has been shown that the performance of WPCs as a structural material depends mainly on the quality of the stress transfer at the interphase (Lee et al. 2007). The interphase is the region between the fiber and the polymer matrix and poor interaction between the two materials reduces the adhesion between them (Niska and Sain 2008). Improvement of the interphase adhesion improves WPC properties, such as tensile strength, toughness, impact, rate of water absorption and others. Consequently, a better understanding of the interfacial properties and characteristics will help to evaluate the overall properties of WPCs (Lee et al. 2007). In this regard, many analytical methods like Atomic Force Microscopy (AFM), contact angle determination, scanning electron microscope (SEM), Fourier transform infrared (FTIR) spectroscopy, dynamic mechanical thermal analysis (DMTA) and others have been used to study the microscopic and macroscopic mechanical, physical and chemical properties of WPCs (Lee et al. 2007; Stark and Matuana 2007; Awaja et al. 2009).

One useful analytical method is chemical force microscopy (CFM), which is an extension of the atomic force microscopy, in which the tip is modified with specific functional groups to provide information about the chemical composition of the surface (Bastidas et al. 2005). CFM was used to study the adhesive forces on cellulose films and bleached softwood kraft pulp fibers in aqueous media by Bastidas et al (2005). They found that the magnitude of the pull-off forces between modified tips and the fiber surface were comparable with results obtained from model cellulose surfaces. Klash et al (2010) also used CFM to determine cellulose and lignin content on fiber surface of several eucalyptus species from South Africa and found significant differences in cellulose and lignin content on fiber surfaces based on site and genotype. Using CFM, Basson (2013) found high interactions between coated tips and cellulose, lignin and compatibilizer substrates. CFM can therefore be used to analyse and quantify the chemical interactions between the different components in WPCs on the micro scale, to help to explain physical and mechanical properties of the macroscopic composite material. Since the surface

characteristics of the wood component and the interfacial properties between the wood and plastic, influence the mechanical and physical properties of WPCs (Shebani et al. 2009).

In South Africa, alien invasive species (AIS), are defined as species that originate from other countries and often out-compete the original vegetation. There are 559 AIS in South Africa of which 383 are plants which are causing damage worth millions of Rands to South Africa's economy every year. Invasive Species South Africa estimates that invasive plants cover up to 10% of South Africa (ISSA 2016). These species need to be cleared from public land and can therefore also be regarded as waste materials. Using them as raw material for WPCs can be regarded as environmentally friendly value adding to a waste material. Most of the woody species are, however, hardwoods with quite different properties compared to the softwoods typically used in WPC systems.

In this study, the adhesive forces determined between AFM tips functionalised with three different compatibilizers and the different wood substrates were determined and related to macroscopic properties of WPCs in an attempt to explain the mechanical properties, such as tensile strength, of WPCs as well as to determine the feasibility to use alien invasive wood species from South Africa for the production of WPCs with the most suitable compatibilizer.

MATERIALS AND METHODS

Materials

LDPE from Sasol Polymers with melt flow index (MFI) value 65g/10min was used as matrix polymer for the WPCs. As compatibilizers the commercially available EVOH and PE-g-MA, both from Sigma-Aldrich, were used as well as thermally degraded LDPE (dPE), which was produced at the Department of Chemistry and Polymer Science, Stellenbosch University. The LDPE was thermally degraded in a forced-air laboratory oven at 90 ^{o}C for 7 weeks (Ndlovu et al. 2013).

The wood fibers were obtained from six invasive tree species, namely Pine (*P. radiata*), Eucalyptus (*E. grandis*), Black wattle (*Acacia mearnsii*), Long-leaved wattle (*A. longifolia*), Port Jackson (*A. saligna*) and Beefwood (*Casuarina cunninghamiana*). Extractives were obtained from a typical softwood (pine) and hardwood (eucalyptus) and no further distinction was made with regards to their composition. The wood was obtained from one softwood (pine) and five invasive hardwood species and their properties are listed in Table 1. The wood species

differ significantly in their chemical and physical properties. Pine, a softwood with uniform, long tracheids and no large pores is similar to other softwood species, which are commonly used for WPC production, while the other wood species are porous hardwood species with significantly different cell types and structure. Hardwoods contain shorter fibers, vessel elements, parenchyma cells and ray cells, resulting in a very inhomogeneous surface (Hodzic and Shanks 2014).

Table 1 Chemical compositions and dimension of softwood and hardwood fibers (Hodzic and Shanks 2014).

Species	Wood type	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)	Aspect ratio (μm)
Pine Eucalyptus Black Wattle	Softwood	40-45	25-30	26-34	0-5	50-200
L-L Wattle Port Jackson Beefwood	Hardwood	45-50	21-35	22-30	0-10	28-86

Wood sections and fibers

Blocks of clear wood with the dimensions of 15 mm ×15 mm × 15 mm were prepared from each wood species and 20 μm thick sections were cut along the grain with Leica RM 2245 rotary microtome with a 16 cm steel blade.

The wood flour for the WPCs was obtained from chipped wood that was subsequently milled in a Drotsky hammer mill with a 4 mm screen. After drying the particles were screened for size and the 180 μm fraction was used for all WPC blends.

Functionalized AFM tips

Silicon force modulation cantilevers from Nanosensors (Switzerland) were used for the tip modifications according to Bastidas et al. (2005) and coated with the following compatibilizers:

- EVOH (Sigma-Aldrich)
- PE-g-MA (Sigma-Aldrich)
- dPE

The silicon tips were first gold coated with an Edwards S150A Gold Sputter Coater and cleaned under a 254 nm UV lamp for 1 hour to ensure that all organic material was removed. A 1 mM thiol solution of 11-mercapto-1-undecanol, 1-octadecanethiol and11-mercapto undecanoic acid (Sigma-Aldrich) in ethanol (KIMIX) was prepared, into which the gold tips were submerged for 2 h at room temperature under Argon gas (Bastidas et al. 2005). A 2 mM solution of each compatibilizer was prepared in xylene or DMSO (EVOH) at 40 ^{o}C into which the thiol coated tips were dipped for 2 h to prepare functionalized tips with PE-g-MA, EVOH and dPE, respectively. The coated tips were then rinsed with n-heptane (KIMIX) and alcohol, and dried in an argon stream (Basson 2013).

WPC compounding

Optimization of ratios

Initially, composites with varying amounts of wood and compatibilizer were prepared with pine as a reference species, in order to determine the optimum ratio and wood loading for each compatibilizer, as their optimum amount may potentially differ. Composite materials of 5 g total mass were compounded in two replicates by melt mixing. The wood content was 30 wt. %, 40 wt. % and 50 wt. %. This was done in order to determine and compare the optimum wood loading. The compatibilizer ratios were 5, 7 and 10 wt % of the polymer part. Stabilizer (2 wt % of the polymer part) was added to prevent degradation. The optimum polymer/wood ratios were found to be 70/30 with 7% EVOH compatibilizer, 70/30 with 10% dPE compatibilizer and 50/50 with 10% PE-g-MA compatibilizer. The formulation was based on a U.S. Patent (No. 6,942,829), which suggests possible ranges of about 20 to 80 wt% of a thermoplastic polymer, about 20 to 80 wt% of a cellulosic filler material and 0.1% to 10 wt% of additives (Drabeck et al. 2005). It is known that not all compatibilizers have the same effect on WPC performance.

WPC processing

In a second step, composite samples were prepared by dissolving the LDPE in 80 mL xylene at 140 °C and then adding the stabilizer and wood flour into the solution while stirring on a hot plate. The solution was stirred and cooled to room temperature, which was followed by precipitation in acetone. The samples were then filtered (150 ml Buchner funnel filter; Sinta Glass) and allowed to dry in a constant air flow at room temperature for three days and conditioned awaiting molding.

Injection molding

Composite samples were moulded into tensile bars ("dog bone") in accordance with ASTM D638 (ASTM 2010) with a HAAKE Mini Jet II from Thermo Scientific (type 557-2290). Five samples were prepared of each group for tensile testing. The samples were conditioned in a climate chamber at 20 ± 3 ºC and relative humidity of 65% prior to testing.

Adhesive force determination with CFM

The CFM measurements were performed on an Easy Scan 2 AFM from Nanosurf (Switzerland) in the force modulation imaging and spectroscopy modes. Force modulation cantilevers with a 2 N/m spring constant from Nanosensors were used and the tips were chemically modified as described above. In order to achieve results describing the entire sample with statistical relevance, 150 force-distance curves were measured at 15 different positions on each sample and outliners eliminated to determine the average adhesive force between the modified tip and sample surface. All CFM measurements were carried out in air
at ambient conditions of 23 ± 2 ºC and 65 ± 2% RH.

Physical properties

The moisture content of each WPC after conditioning for several weeks at 20ºC and 65% RH was measured by the oven-dry method according to ASTM D-4442 (ASTM 2007) using equation 1:

$$MC\ (\%) = \frac{Initial\ mass - ovendry\ mass}{ovendry\ mass} \times 100 \qquad (1)$$

The density was determined by volume measurement in accordance with ASTM D-2395 (ASTM 2014) and calculated with equation 2:

$$\rho = \frac{ovendry\ mass}{green\ Volume} \times 100 \qquad (2)$$

Mechanical properties

The tensile strength was determined on an LRX (LLOYD instruments) universal tensile tester in accordance with ASTM D638 (ASTM 2010). A preload of 30 N was applied at a cross-head speed of 50 mm/min. Five dumbbell shaped samples were analysed for each WPC formulation

to obtain average values. The gauge size of the samples was 15.26 mm long, 3.03 mm wide and 0.76 mm thick. The stress and elongation tensile modulus at maximum load was calculated from the stress strain curves and average values with standard deviations are reported.

Statistical Analysis

Statistical analysis was conducted using the Origin 8.5.1 software in combination with a one-way analysis variance (ANOVA). A Tukey HSD Test was used to test the statistical significance at 0.05 % probability level. To understand the relationship among the variables, regression analysis was conducted.

RESULTS AND DISCUSSION

Adhesion forces

To understand how well the three main components forming the WPC bond to each other, chemically functionalized tips were used to quantify the adhesive force between the compatibilizer coated AFM tips, the polymer and the different wood surfaces.

The average interaction forces between the coated tips and an LDPE model film were 210.3 ± 57.71 nN for EVOH, 227.9 ± 92.07 Nn for PE-g-MA and 215.97 ± 60.56 nN for dPE. No significant differences ($p < 0.05$) were found between the results regarding the interaction between compatibiliser and LDPE.

Results of the interaction between compatibilizer coated tips and the wood surfaces are displayed in Figure 1a. The EVOH coated tip showed the highest adhesion on Pine and the lowest on Black wattle. The adhesive forces ranged from 200 to about 300 nN. The PE-g-MA coated tip showed the least variation and sensitivity on all the species and adhesion forces ranged from 200 to 250 nN. The dPE coated tip exhibited the lowest adhesive forces around 100 nN with very small inter and intra-sample variation.

Based on the experimental evidence, the large variation of the adhesive force measurements can be explained by the varied surface structure of the wood surfaces, chemical and anatomical differences between the species (Stokke and Gardner 2003). Over the scan range of about 100 μm^2, the chemical composition of the fiber surface and the cell type may change drastically, to result in a large range of adhesive forces determined between the functional groups of the

compatibilizer and the wood surface, which are measured on a point the size of a few molecules.

Tips functionalized with dPE showed little variation on different wood species and although the adhesive force is generally lower than that measured between the other compatibilizers and wood substrates, it seems less sensitive to changes caused by the wood filler.

The analysis of variance (ANOVA) presented in Table 2 showed significant differences between the adhesive forces observed between the compatibilizer coated tips and the wood substrates. For the EVOH coated tip, pine and eucalyptus were statistically different ($p < 0.05$) from the other species. For the PE-g-MA coated tip significant differences were found between pine, long-leaved wattle and Port Jackson, while there were no significant differences between all the species for the dPE coated tip.

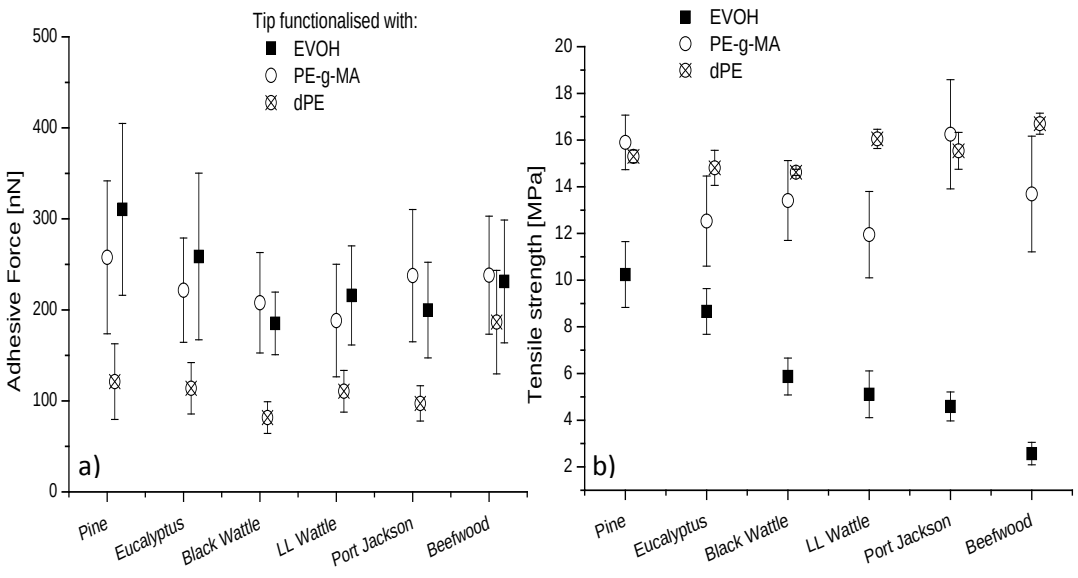

Figure 1a: Adhesive forces between compatibilizer coated tips and various wood surfaces; b: Tensile strength of WPCs with different compatibilizers and wood species.

Physical properties

Moisture content and density are some of the most important factors that affect the properties of WPCs and they are listed in Table 2. The highest MC (27%) was observed for Beefwood and the lowest for Eucalyptus (5%) composites containing EVOH as compatibilizer. The MC for PE-g-MA composites ranged from 4-5 % for the different composites. The results of an ANOVA indicated no significant difference ($p < 0.05$) between the wood species. Composites

made with dPE had the lowest MC, ranging from 2-4 %. Apart from Pine, there was no significant difference ($p < 0.05$) between the other species. The high MC of EVOH composites negatively affects the properties of the WPC. The measured MCs were all higher than those determined in commercial WPCs, such as Geodeck boards, which have an MC of 1.7 % (Klyosov 2007).

The densities were similar for PE-g-MA and dPE composites, whilst EVOH composites had a slightly lower, but comparable density. The similar densities were obtained because the WPCs were formulated based on weight. There were no significant differences ($p < 0.05$) between the species for the dPE composites and a few differences between the PE-g-MA and EVOH composites, as shown in Table 2.

The measured densities compare very well to the densities of commercial products, such as, for example, Boardwalk, Trex, Monarch and Rhino Deck WPCs with densities of 0.91 – 0.96 g/cm^3 (Klyosov 2007).

Table 2 shows the physical, mechanical properties and adhesive forces of various WPCs from six species with three compatibilizers.

Table 2: Physical, mechanical properties and Adhesive forces of various WPCs from six species with three compatibilizers

		Pine	Euc.	Black W.	LL. wattle	PJ.	Beef wood
EVOH	Tensile strength	10.24^{a} (1.41)	8.66^{b} (0.98)	5.87^{cab} (0.79)	5.11^{dab} (1)	4.59^{eab} (0.62)	2.57^{fabcde} (0.48)
	Density	0.74^{a} (0.03)	0.83^{ba} (0.02)	0.78^{ca} (0.05)	0.8^{da} (0.02)	0.71^{ebcd} (0.01)	0.7^{fbcd} (0.03)
	MC	15.84^{a} (4.23)	5.06^{ba} (0.99)	8.39^{ca} (3.17)	10.99^{dab} (3.52)	20.19^{ebcd} (2.78)	26.87^{fabcde} (2.4)
	Adhesive force	310.49 ^{a} (94.44)	258.68^{ba} (91.58)	185.18^{cab} (34.4)	215.92^{dabc} (54.47)	199.75^{eab} (52.53)	231.25^{face} (67.5)
PE-g-MA	Tensile strength	15.9^{a} (1.17)	12.53 (1.93)	13.41 (1.71)	11.95^{da} (1.85)	16.25^{ed} (2.34)	13.69 (2.48)
	Density	0.95^{a} (0.02)	0.97 (0.01)	0.99^{ca} (0.02)	0.98^{da} (0.01)	0.99^{ea} (0.01)	0.98^{fa} (0.01)
	MC	5.32 (1.72)	4.31 (0.99)	4.2 (0.36)	4.36 (1.09)	4.25 (0.13)	4.27 (0.16)
	Adhesive force	257.75^{a} (84.03)	221.67^{ba} (57.27)	207.86^{ca} (55.2)	188.3^{dab} (61.82)	237.64^{ecd} (72.69)	238.16^{ecd} (64.88)
dPE	Tensile strength	15.3^{a} (0.27)	14.81^{b} (0.75)	14.62^{c} (0.13)	16.05^{dbc} (0.41)	15.54^{e} (0.79)	16.7^{fabce} (0.45)
	Density	0.92 (0.01)	0.91 (0.01)	0.91 (0.01)	0.92 (0.01)	0.91 (0.01)	0.91 (0.01)
	MC	3.73^{a} (1.18)	2.09^{ba} (0.11)	2.17^{ca} (0.29)	2.3^{da} (0.13)	2.35^{ea} (0.06)	2.42^{fa} (0.3)
	Adhesive force	121.17^{a} (41.61)	113.84 (28.23)	81.68 (17.48)	110.63 (22.93)	97.24 (19.35)	186.55 (56.84)

Values within the same line row by same letters are significantly different at $\alpha = 0.05$

Standard deviation in brackets

Tensile strength

Figure 1b shows the tensile strength of composites made with LDPE, different compatibilizers and different wood species.

The EVOH composites showed high tensile strength of about 10 MPa in composites containing Pine and Eucalyptus. All other composites had significantly lower tensile strength, with only about 2 MPa in the Beefwood composite. This shows that EVOH as compatibilizer is highly sensitive to its binding partners and does not work well on all wood species. This can be explained by the fact that EVOH does not interact with all parts of the polymer and therefore counteracts the positive reinforcement effect of the fibers, as described by Basson (2013). Furthermore, EVOH only facilitates interactions between the ethylene-rich areas of the LDPE and wood (Drummond et al. 2000). The tensile strength was further decreased by the high MC of EVOH composites. The tensile strength corresponds to the results obtained in the CFM analysis, where the adhesive forces detected between EVOH and wood were very variable with the wood species.

The composites containing PE-g-MA as compatibilizer had significantly a higher tensile strength between 12 and 16 MPa, with less variation and sensitivity towards the wood species. The dPE compatibilizer produced the highest tensile strength results of around 15 to 16 MPa for all wood species. This is an indication that the dPE compatibilizer is equally compatible with all the wood species, which is again in good agreement with the adhesive force results obtained by CFM (Ndlovu et al. 2013).

The analysis of variance (ANOVA) presented in Table 2 showed significant differences ($p < 0.05$) between tensile strength of most the wood species for EVOH composites. WPCs containing PE-g-MA showed the least differences, only Pine and Long-leaved wattle and Long-leaved wattle and Port Jackson were significantly different. Wood species in dPE composites did not show significantly different tensile strength.

The tensile strength of the WPCs determined in this study compares well with commercial WPCs, for example, products of TimberTech, GeoDeck, Trex, EverX and Timberlast which have tensile strength values of 8-13 MPa (Klyosov 2007).

Relationship between microscopic and macroscopic properties

To determine the relationship between physical and mechanical properties of WPCs, a linear regression model was fitted and the results are presented in Figure 2.

Figure 2a shows that the density accounted for 22 % of the tensile strength for the EVOH composites, and only 4 % for PE-g-MA and dPE composites, respectively. This shows that that the prediction rate between density and tensile strength is low for all composites, but especially for PE-g-MA and dPE WPCs.

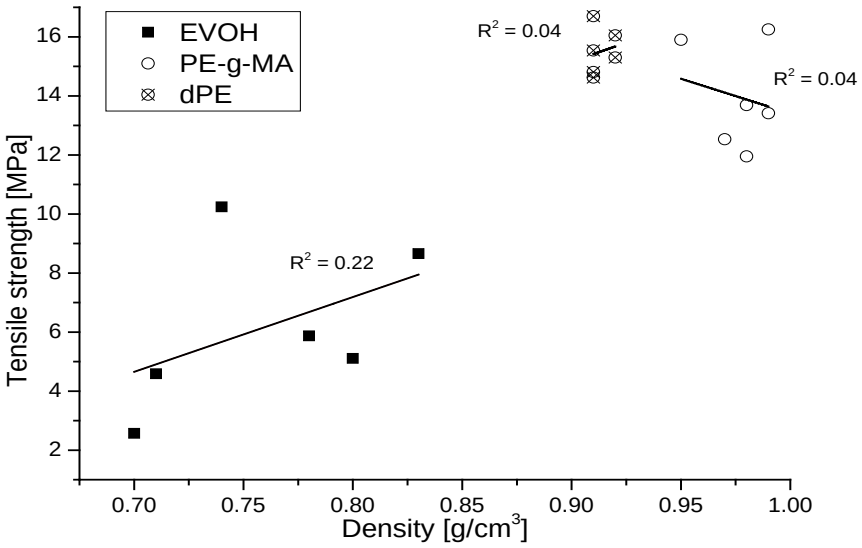

Figure 2a Relationship between density and tensile strength of WPCs

The model between moisture content and tensile strength of the WPCs fitted well for two of the compatibilizers with R^2 of 0.34 for EVOH and 0.23 for PE-g-MA and normal for dPE with R^2 of 0.002. It can be seen that the lower the moisture content the better the tensile strength. The relationship between moisture content and tensile strength is shown in Figure 2b.

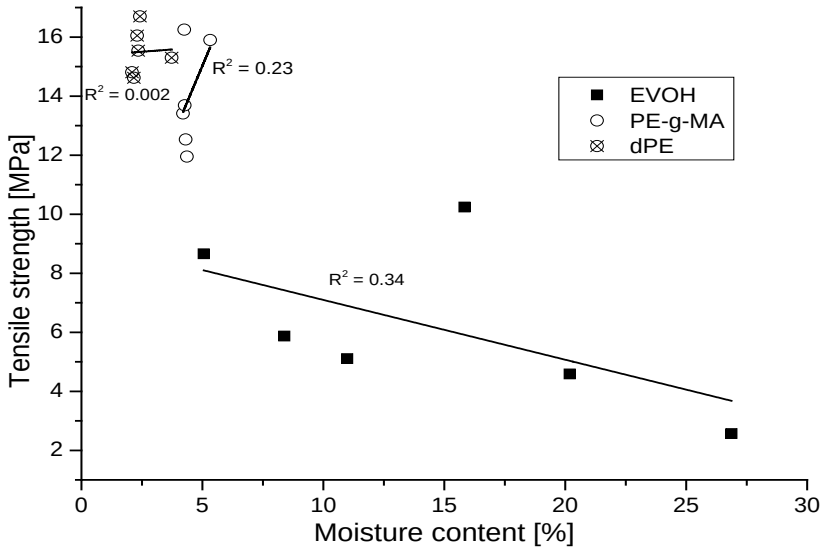

Figure 2b Relationship between moisture content and tensile strength

The density contributed hardly to the adhesive force, for EVOH (0.1 %) and dPE (0.3%) composites, while it accounted for 28 % of the adhesive force in PE-g-MA composiets. It can be seen in Figure 2c that for EVOH composites a higher density leads to a higher adhesive force, whereas for PE-g-MA and dPE a higher density leads to lower adhesive force.

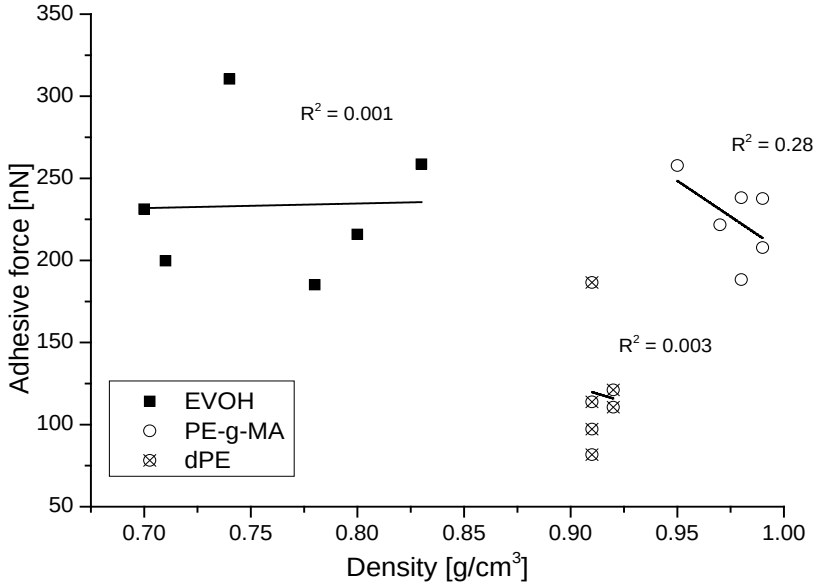

Figure 2c Relationship between density and adhesive force between compatibilizer coated tips and wood surfaces.

Figure 2d shows the relationship between the tensile strength of WPCs and the adhesive force. The determined R^2 values were 0.43 for EVOH, 0.54 for dPE and 0.58 for PE-g-MA composites. This means that the tensile strength can be explained by the adhesive forces acting between compatibilizer and wood to the extent of about 50%.

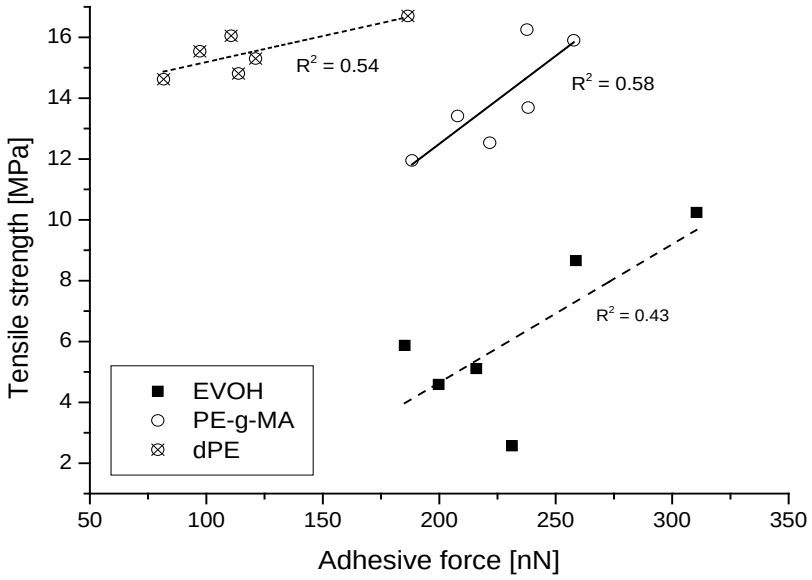

Figure 2d: Relationship between tensile strength and adhesive force between compatibilizer coated tips and wood surfaces.

Figure 2 shows that the relationship between some of the variables is low, yet important conclusions can be drawn from the statistically significant ($p < 0.5$) differences that were observed.

The highest adhesive force interaction with the EVOH coated tip was observed on Pine wood followed by Eucalyptus, a softwood and a hardwood. All acacias and the Beefwood resulted in lower adhesive forces. The tensile strength changed more significantly ($p < 0.05$) with the wood species. The highest value was observed in the Pine composite and the lowest in the Beefwood composite. The MC was very high for most of the WPCs containing EVOH as compatibiliser and the density differed between the species.

The PE-g-MA coated tip showed less difference in adhesive forces on the different wood species than the EVOH coated tip, with a slight decrease in adhesive force for some of the hardwoods. The tensile strength of composites containing PE-g-MA was generally much higher with few significant ($p < 0.05$) differences detected between the wood species. The adhesive

force and the tensile strength of PE-g-MA composites did not follow the same trend, but the lowest adhesive force and the lowest tensile strength were determined in composites made from Long-leaved wattle and the highest adhesive force and tensile strength in the composite made from Pine. The MC and density were similar for all the WPCs containing PE-g-MA as compatibilizer with few differences among them.

The dPE coated tip showed a lower adhesive force with some variations on all the wood species, which can be explained by chemical and anatomical effects of the wood species. Likewise, the tensile strength of all WPCs containing dPE as compatibilizer was similar with little variation. The composites containing dPE had the lowest adhesive forces determined by CFM, but the highest tensile strength in the composites. This can be explained by the fact that dPE binds well to the matrix and more importantly shows only a small variation on the wood surfaces (independent of cell type or surface chemistry), whereas the large variation of the EVOH compatibilizer proved that there were binding sites with high adhesion, but also sites with no affinity at all as a result of the heterogeneous nature of the wood surface. This heterogeneous nature of the wood surface leads to variations in interfacial interactions that may have impacted negatively on the mechanical performance of the composites (Petinakis et al. 2014).

CONCLUSIONS

The performance of WPCs containing EVOH, PE-g-MA and dPE and different wood species in LDPE matrix was investigated on a micro and macroscopic scale. The high MC of EVOH composites negatively affected and lowered tensile strength of the final WPC. The EVOH composites were found to have high tensile strengths with Pine and Eucalyptus wood, however, EVOH proved to be very sensitive to the wood species and did not perform well with the other wood species. Composites containing PE-g-MA had higher tensile strength and the results varied less with the wood species. Composites containing dPE as compatibilizer had a high tensile strength for all investigated species and the values were comparable to the WPCs containing PE-g-MA. The densities and tensile strengths of this study compare well with some commercial WPCs. The results are difficult to relate, as many factors, such as the wood species, MC, density, compatibilizer and processing method affect the performance of the final product. However, the microscopic properties significantly affect the macroscopic properties of the WPCs.

In conclusion, the study shows that the studied invasive wood species may be incorporated into WPCs if the correct compatibilizer is chosen. dPE proved to be the best choice, as it had the lowest sensitivity to the wood species and yielded WPCs with high mechanical strength. Furthermore, it is an inexpensive compatibilizer that can potentially be obtained from waste materials, just like the polymer matrix.

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Chapter Six

Mechanical properties of wood plastic composites made from various wood species with different compatibilisers

Summary

Alien invasive species (AIS) are posing a serious and direct threat to biodiversity, water security and productive use of land in South Africa. Most of these species need to be cleared and are therefore regarded as waste material, which could become raw material for wood plastic composites (WPCs). This part of the study evaluates the mechanical properties of WPCs made from LDPE, various invasive wood species from South Africa and three different compatibilisers. The tensile strength, tensile modulus, elongation at break and impact strength were analysed to determine the feasibility of utilising alien invasive species for the production of WPCs, as well as the use of a new compatibiliser based on degraded LDPE.

WPCs containing wood from *Pinus radiats* (Pine), *Eucalyptus grandis* (eucalyptus), *Acacia mearnsii* (black wattle), *Acacia longifolia* (long-leaved wattle), *Acacia saligna* (Port Jackson) and *Casuarina cunninghamiana* (beefwood), low density polyethylene (LDPE) and three different compatibilisers, namely poly(ethylene-vinyl-co-alcohol) (EVOH), poly(ethylene-graft-maleic anhydride) (PE-g-MA) and thermally degraded LDPE (dPE) were produced. EVOH was used due to its affinity with PE, as well as its ability to form hydrogen bonds with cellulose. PE-g-MA was chosen, because of its active ring-anhydride group, which can easily react with the hydroxyl groups on the wood surface and thermally degraded LDPE (dPE) is a novel and inexpensive compatibiliser developed at the Department of Chemistry and Polymer Science. The samples were compounded by melt mixing and molded into tensile bars by injection. Tensile modulus, tensile strength, elongation at break and impact strength were determined according to ASTM standards.

Composites with PE-g-MA as compatibiliser showed the highest tensile modulus for all wood species. EVOH composites were less rigid with a low tensile modulus for all wood species. The tensile modulus of composites without compatibiliser increased significantly with increased wood loading for most of the species, thus more wood provided more rigid composites, which require higher stress to break. Composites containing PE-g-MA and dPE had a high tensile

strength, whereas composites containing EVOH proved to be inferior. Composites with PE-g-MA as compatibiliser showed the lowest elongation at break compared to other composites, for all wood species but Pine. The addition of compatibilisers improved the impact strength of most of the composites. The mechanical performance of the composites improved when PE-g-MA or dPE compatibilisers were added, whereas EVOH as compatibiliser tended to yield inferior results. The study proved that the investigated invasive wood species - mostly hardwoods - can be incorporated into WPCs. It was also shown that dPE, a novel and inexpensive compatibiliser that can be sourced from waste materials, is an effective adhesion promoter in WPCs independent of the wood species used.

Mechanical properties of wood plastic composites made from various wood species with different compatibilisers

Bernard Effah[1], Albert Van Reenen[2] and Martina Meincken[1*]

[1]Department of Forest and Wood Science, Stellenbosch University, South Africa

[2]Department of Chemistry and Polymer Science, Stellenbosch University, South Africa

Email: mmein@sun.ac.za

Abstract

Wood plastic composites (WPCs) were prepared containing wood from six different tree species invasive to South Africa, low density polyethylene (LDPE) and three different compatibilisers, namely poly(ethylene-co- vinyl alcohol) (EVOH), poly(ethylene-graft-maleic anhydride) (PE-g-MA) and thermally degraded LDPE (dPE). Tensile modulus, tensile strength, elongation at break and impact strength were determined. The tensile modulus of compatibilised composites was high with PE-g-MA and low for EVOH for all the species, while it increased significantly with increasing wood load for most uncompatibilised composites.

Composites containing PE-g-MA and dPE had a high tensile strength, whereas composites containing EVOH proved to be inferior. Composites with PE-g-MA as compatibiliser showed the lowest elongation at break compared to other composites, for all wood species but pine. The addition of compatibilisers improved the impact strength of most of the composites. The mechanical performance of the composites improved when PE-g-MA or dPE compatibilisers were added, whereas EVOH as compatibiliser tended to yield inferior results. The study proved that the investigated invasive wood species – mostly hardwoods - can be incorporated into WPCs. It was shown that dPE, a novel and inexpensive compatibiliser that can be sourced from waste materials, is an effective adhesion promoter in WPCs independent of the wood species used.

1 Introduction

There has been growing interest in the use of natural cellulosic fibres as reinforcement for polymeric matrices. Adding natural fibres to plastics provides a cost reduction and improves the physical and mechanical properties (Kim and Pal 2010; Stokke et al. 2013; Hodzic and Shanks 2014). Wood plastic composites (WPCs) made from wood fibres and polymers are enjoying rapid growth in applications replacing wood (Wechsler and Hiziroglu 2007; UO and Rizvi 2008; Miléo et al. 2015). Composite materials are combination of two or more materials with different properties and different forms that are compounded in a way that retains the key features of the original components in addition to new characteristics, not possessed by any of the original components as a result of the combined effects (Kim and Pal 2010; Youngquist and Rowell 1989; Wang et al. 2011). The greatest growth potential for WPCs lies in building products that have limited structural requirements, such as decking, fencing, industrial flooring, landscape timbers, railings, mouldings, furniture, consumer goods, packaging, automotive, marine and roofing (Caulfield et al. 2005; Stark and Matuana 2007; Mohanty et al. 2005; Li et al. 2013).

Natural fibres (wood) as fillers in polymer composites are used because it is economical, low in processing energy, they have lower density, UV resistance, moderately high stiffness, less abrasiveness to equipment, are renewable and biodegradable (Stokke and Gardner 2003; Youngquist and Rowell 1989; Harper and Wolcott 2004). However, there is typically a poor fibre-matrix interfacial adhesion as a result of surface incompatibility between polar natural fibres and non-polar polymers. To overcome this, a compatibiliser is often used to improve interfacial bonding of the two different phases (Kalita and Netravali 2015; Balasuriya et al. 2001; Rowell 2007; Spiridon 2014).

Compatibilisers have a polar and non-polar end, which attaches to the wood fibre and polymer, respectively. Their primary function is to improve the homogeneity of dissimilar or incompatible materials, as lack of homogeneity can reduce the mechanical properties of the end product (Niska and Sain 2008). Poly(ethylene vinyl-co-alcohol) (EVOH) and Polyethylene-graft-maleic anhydride (PE-g-MA) are some of the conventionally used compatibilisers for WPCs. The ethylene-vinyl in EVOH attaches to the polymer matrix and the alcohol to the wood surface. PE-g-MA is based on ethylene, which binds to the polymer matrix, with maleic anhydride (MA) grafted onto it, which attaches to wood surface. Figure 1 shows the coupling mechanism of a typical compatibiliser – in this case MA grafted to polypropylene. Thermally

degraded LDPE (dPE) has also proven to be a suitable compatibiliser for WPCs. When LDPE undergoes thermooxidative degradation, carbonyl and hydroxide groups are produced and the new functional groups allow the polymer to be used as a compatibiliser for WPCs (Ndlovu et al. 2013).

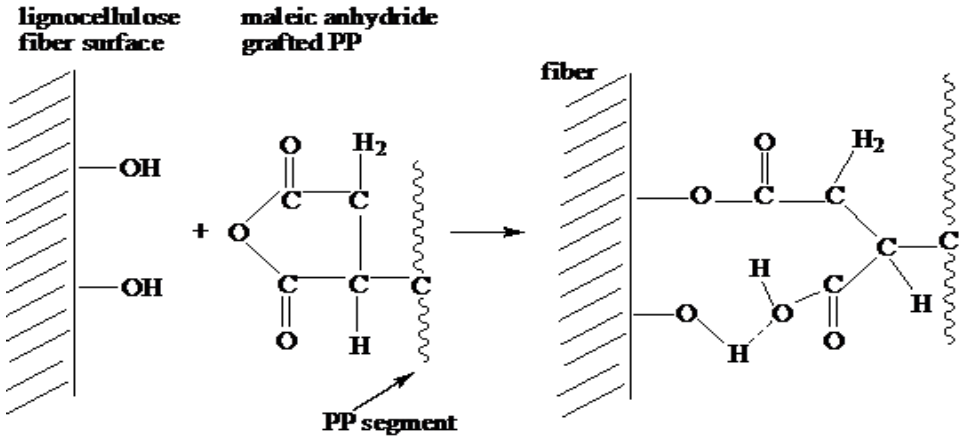

Figure 1 Reaction mechanisms of MAPP with a hydroxyl group on the surface of the wood flour (Ndiaye et al. 2011).

The polymeric compatibilising agent attaches with one end to the polymer matrix through physical interaction and/or chemical bonds and reacts with the other end with the filler particles (Bicerano 2005).

The polymer matrix of WPCs frequently comprises polyolefins, such as polyethylene (PE), polypropylene (PP), or polyvinyl chloride (PVC) (Abdelaal et al. 2012; Sihombing et al. 2012) whereas the wood fillers are typically softwood particles that consist of long, uniform fibres with a well-known chemical composition.

In South Africa, alien invasive species (AIS), are defined as species that originate from other countries and out-compete the original vegetation. There are 383 AIS in South Africa of which 110 are woody trees/shrubs, which are causing damage worth millions of dollars to South Africa's economy every year. Species of invading alien plants cover 8% of South Africa's surface area (Macdonald et al. 2003) and need to be cleared from public land. They can therefore be regarded as waste material and using them as raw material for WPCs can be regarded as an environmentally friendly way of value adding to a waste material. It is, however, not clear how the different wood/fibre properties of the AIS impact on the properties of WPCs.

The mechanical properties of wood-plastic composites, such as strength, impact resistance, hardness and stiffness play an important role in deciding the suitability of WPC products for various applications (Ndiaye et al. 2011). The structure, nature, configuration, interaction and the relative content of the three phases of the composite determine the performance of the composite material (Wang et al. 2011). The properties of WPCs depend on the volume fraction of wood in the composite, the processing temperature, additives and type of plastic used (Rowell 2007). Elkhaoulani et al. (2013) studied the mechanical properties of composite based on natural fibres and found that the tensile strength stabilised when a coupling agent was used. Ndlovu et al. (2013) studied LDPE-wood composites with thermally degraded LDPE (dPE) as compatibiliser and reported that the dPE influenced the mechanical properties of the composites positively. Li et al. (2013) studied the effects of compatibilisers on composites of acorn shell powder and LDPE. The results showed that compatibilisers improved the mechanical properties of the composites at different levels, with PE-g-MA being the best performing compatibiliser. Kim et al. (2006) evaluated saw dust-reinforced LDPE composites with EVOH as compatibiliser. They found EVOH to be a good adhesion promoter for WPCs, which improved the mechanical properties of the composites significantly. The effects of coconut fibre content on the tensile, thermal, structural, and biodegradability properties of starch/EVOH/glycerol blends were characterized by Rosa et al. (2009). They concluded that low fibre content blends were more flexible with higher tensile strength than composites with higher fibre ratios and that EVOH was a suitable compatibiliser.

In related work, Gozdecki et al. (2011) studied the effect of particle size and specimen cross-sectional size on the mechanical properties of wood-PE composites. They observed that tensile, flexural and impact strengths increased with increasing particle size, whilst the same properties decreased with increasing specimen cross-section. Similarly, Kord (2011) investigated the effect of MA on the mechanical properties of WPCs based on PP and sawdust. His results indicated that the mechanical properties of the composites improved with the addition of a MA compatibiliser. Bledzki et al. (2002) studied the physico-mechanical properties of wood fibre reinforced composites and observed an increase in tensile and impact strength when MAPP was used as compatibiliser.

In this study the mechanical properties of WPCs made from LDPE, various invasive wood species from South Africa and three different compatibilisers are compared. The tensile

modulus, tensile strength, elongation at break and impact strength were analysed. The objective was twofold; firstly, to investigate the suitability of six AIS as wood fillers for WPCs and secondly the relative comparison of different compatibilisers and their effect on the mechanical properties of WPCs made with six AIS species.

2 Materials and methods

2.1.1 Materials

EVOH, PE-g-MA and dPE were selected as compatibilisers. EVOH was selected, because it has some affinity with PE, as well as its ability to form hydrogen bonds with cellulose. PE-g-MA was chosen because of its active ring-anhydride group, which can easily react with the hydroxyl groups on the wood surface. Thermally degraded LDPE (dPE) is a novel and inexpensive compatibiliser currently investigated in various ongoing research projects in our group. LDPE from Sasol Polymers with a melt flow index of 65g/10 min was used as matrix polymer. EVOH and PE-g-MA were obtained from Sigma-Aldrich and dPE was obtained from LDPE heated in a laboratory oven at 90^{o}C for 7 weeks. Irganox + PP_{02}_1stabilizer was supplied by Sasol Polymers.

The wood particles were obtained from six invasive tree species, namely Pine (*Pinus radiata*), Eucalyptus (*Eucalyptus grandis*), Black Wattle (*Acacia mearnsii*), Long-Leaved Wattle (*Acacia longifolia*), Port Jackson (*Acacia saligna*) and Beefwood (*Casuarina cunninghamiana*). Apart from Pine, all species are hardwoods. The wood was chipped and further milled in a Drotsky hammer mill with a 4mm screen and then dried in an oven at 103 ± 2 °C for 24 hours. The particles were screened for size in a Retsch shaker (AS 200). Particles retained in the 180µm sieve were used for the composites.

2.1.2 Particle characteristics

The length and width of 250 randomly selected particles were measured with a Leica EZ 4D optical microscope using the Leica Application Suite (LAS) software at 20x magnification. Since the curing rate of polymer resins might be affected by the pH value of the components, the pH of the wood was determined by an extraction method and measured with a PH 25+ meter (Crison Instruments, S.A). The chemical composition of the species was not determined in this study, but typical values for hard and softwoods are given in Table 1, because they may affect the properties of the WPC system. The average dimensions and pH value, as

well as chemical composition of soft- and hardwoods are given in Table 1.

Table 1 Particle characteristics and chemical composition of wood species ([a]Gellerstedt and Henriksson 2009; [b]Ver Elst and Pieterse 2006; [c]Shebani et al. 2009; [d]Hindi 2012)

Species	pH	Particle sizes			Chemical composition		
		Particle length (mm)	Particle width (mm)	Aspect ratio	Cellulose (%)	Lignin (%)	Extractives (%)
Pine	4.78	0.46	0.11	4.18	40[a]	27.7[a]	3.5[a]
Eucalyptus	4.51	0.39	0.12	3.25	45[a]	31.3[a]	2.8[a]
Black Wattle	4.79	0.47	0.1	4.7	35.67[b]	13.67[b]	9.26[b]
L-L Wattle	4.78	0.49	0.11	4.45	34.67[b]	19.67[b]	8.83[b]
Port Jackson	4.62	0.71	0.14	5.07	38.67[b]	11.5[b]	6.02[b]
Beefwood	6.1	0.82	0.12	6.83	38.11[c]	25.6[d]	13.8[d]

2.2 WPC compounding

2.2.1 Evaluation of optimum blending ratio

In a pilot project, the optimum blending ratio was for each compatibiliser was determined with Pine as a reference species, as previous studies showed that the optimum ratios differ slightly (Shebani et al. 2009). This was done to allow comparison of the systems with the optimum blend for each compatibiliser system and detect the effect of the wood species. The wood content was varied between 30, 40 and 50 wt% and the compatibiliser ratios were 5, 7 and 10 wt % of the polymer part. Stabilizer (2 wt% of the polymer part) was added to prevent degradation.

The optimum polymer/wood ratios were found to be 70/30 with 7% EVOH compatibiliser, 70/30 with 10% dPE compatibiliser and 50/50 with 10% PE-g-MA compatibiliser. These ratios were maintained for all other wood species.

2.2.2 WPC Processing

In a second step, composite samples of 5 g total mass were compounded in two replicates by dissolving the LDPE in 80 mL xylene at 140 °C and then adding the stabilizer and wood flour into the solution while stirring on a hot plate. The solution was stirred and cooled to room temperature, which was followed by precipitation in acetone. The samples were then filtered (150ml Buchner funnel filter; Sinta Glass) and allowed to dry in a constant air flow at room temperature for three days and conditioned.

2.2.3 Injection molding

Samples were moulded into tensile bars ("dog bone" shaped) with a HAAKE Mini Jet II from Thermo Scientific (type 557-2290) according to ASTM D638 (ASTM 2010). Five tensile bars of each composite were prepared for tensile and impact resistance testing. The samples were conditioned for 48 h prior to testing and all the tests were performed at room temperature of 23±2 °C and relative humidity of 65±2 %. The sample dimensions were gauge length 15.26 mm, width 3.03 mm and thickness 0.76 mm. Pure LDPE was used as control to ascertain the performance of the compatibilisers. The following settings were used: Cylinder temperature (180 ºC), mold temperature (90 ºC), injection pressure (250 bar) and post hold pressure (250 bar).

2.3 Mechanical characterisation

2.3.1 Tensile strength

The tensile strength was determined on an LRX (LLOYD instruments) universal tensile tester in accordance with ASTM D638-10 (ASTM 2010). No preload was applied at a cross-head speed of 50 mm/min. Five dumbbell shaped samples were analysed for each WPC formulation to obtain average values. The stress and elongation tensile modulus at maximum load were calculated from the stress strain curves and average values with 95 % confidence intervals are reported. All tests were conducted in ambient conditions.

2.3.2 Impact strength

A CEAST Torino (6546/000) high speed tensile impact tester was used to study the impact strength of the composite samples according to ASTM D-1822 (ASTM 2013). The composite samples were subjected to a 15 Joule hammer weight (type 0.96) at a 90° angle. Five samples were tested to report the average impact strength. The tests were performed in ambient conditions.

2.4 Statistical Analysis

Mean values with error bars representing 95 % confidence intervals were plotted for all mechanical properties. One-way analysis of variance (ANOVA) with a post-hoc Tukey HSD Test was conducted to determine significance of different treatments at a 0.05 % probability level. A p-value of less than 0.05 was considered to describe statistically significant differences.

3 Results and Discussion

3.1 Tensile modulus

Tensile modulus shows a material's ability to deform elastically to an applied stress and is the ratio of stress to elastic strain in tension. A high tensile modulus means that the composite is rigid and more stress is required to produce a given amount of elongation. The tensile modulus of composites with compatibilisers is shown in Figure 2a. Composites containing PE-g-MA as compatibiliser had the highest tensile modulus for all the wood species, however, with a large inter-sample and inter-species variation. Composites containing dPE had a somewhat lower tensile modulus with a low inter-sample variation. The tensile modulus of both PE-g-MA and dPE composites were significantly different from each other on eucalyptus, black wattle, long-leaved wattle and Beefwood composites. The composites containing EVOH as compatibiliser had a significantly lower tensile modulus with a small inter sample variation. The increase in tensile modulus compared to pure LDPE was to be expected, as the wood particles are stiffer than the polymer. Figure 2a shows results of tensile modulus of WPCs with different compatibilisers and wood species.

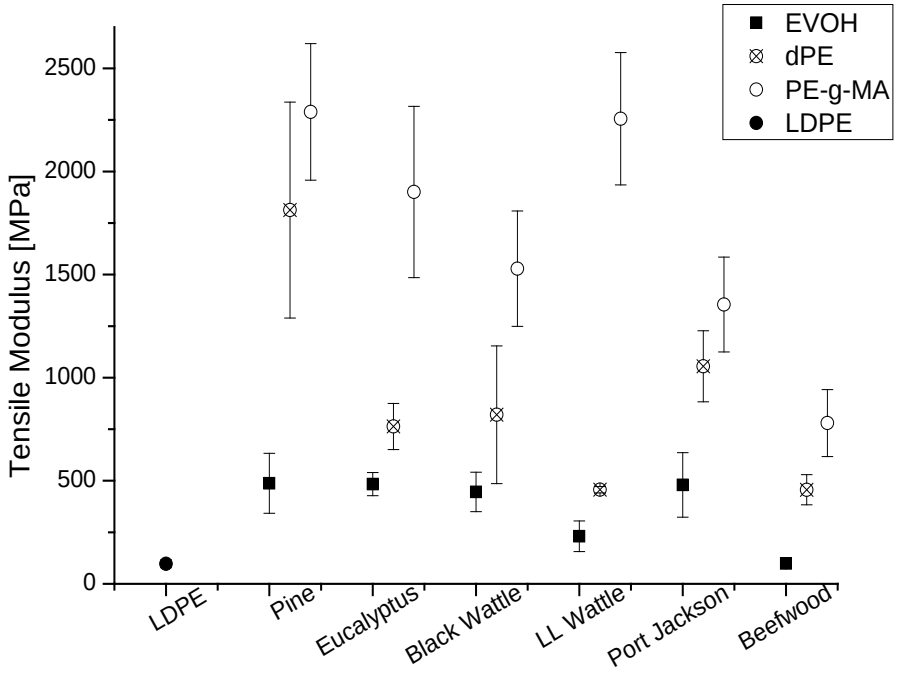

Figure 2a Tensile modulus of WPCs with compatibiliser and different wood species.

The tensile modulus of composites without compatibiliser (Figure 2b) increased significantly with increasing wood load for most of the species with the exception of pine and Beefwood. The highest tensile modulus for both 30 % and 50 % wood loading was found in pine composites. The lowest modulus was observed in long-leaved wattle composites with 30% wood loading and both Beefwood composites, irrespective of the wood loading. The increase in tensile modulus with increased wood loading may be attributed to the stiffness imparted by the wood particles. Sain and Pervaiz (2008) found in their study that increased fibre content led to increased tensile modulus. Similar results were found by Elkhaoulani et al. (2013) and Bledzki et al. (2002).

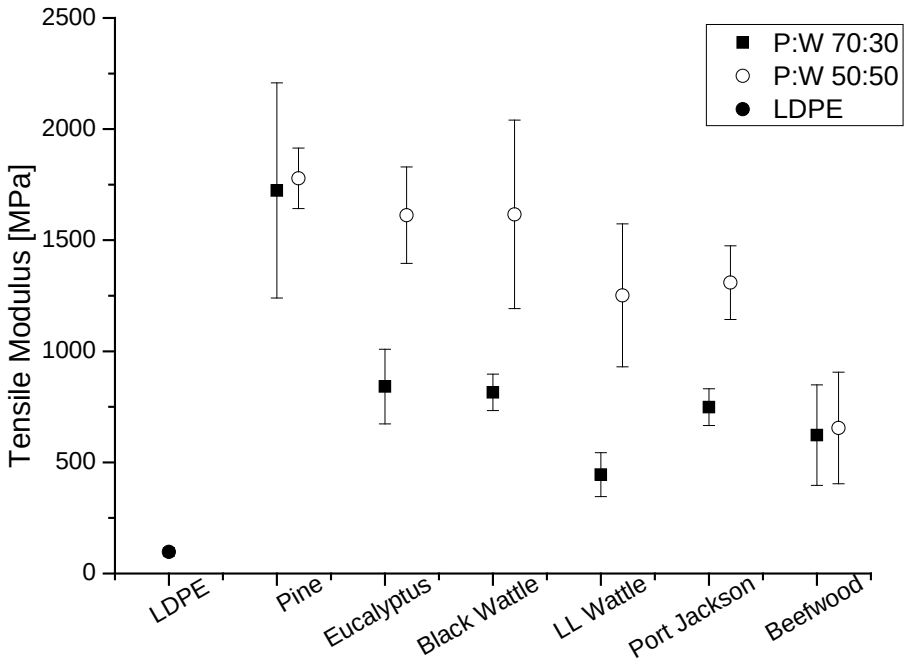

Figure 2b Tensile modulus of WPCs with 30% and 50% wood content of different species without compatibiliser.

It can be seen that incorporation of wood particles increased the stiffness compared to pure LDPE with and without the addition of compatibilisers.

Figure 2a shows that EVOH composites were less rigid than all the uncompatibilised composites or the composites containing other compatibilisers. For both compatibilised and uncompatibilised composites, it could be observed that wood species had effect on the tensile modulus and that Pine composites showed a higher tensile modulus for the 70:30 composites and resulted in stiffer samples than composites containing any of the other hardwood species with the exception of eucalyptus, which can be attributed to the slightly higher (27.7 %) lignin content of Pine, which stiffens the fibres (Walker 2006). The higher the ratio of lignin to cellulose the better the interfacial adhesion that can be achieved since lignin acts as a natural adhesive within the cellulose (Shebani et al. 2009).

3.2 Tensile strength

Figure 3a shows the tensile strength of composites made with compatibilisers, LDPE and different wood species. The EVOH composites showed a good tensile strength of about 10 MPa in composites containing pine and eucalyptus. All other composites had lower tensile strength, with the lowest being only about 2 MPa in the Beefwood composite. This shows that EVOH as compatibiliser is highly sensitive to its binding partners and does not work for all wood species. The composites containing PE-g-MA as compatibiliser had significantly higher tensile strength between 12 and 16 MPa and showed much less sensitivity to the wood species used as filler particles. The variation of tensile values with PE-g-MA compatibiliser is, however, rather large for all wood species. Composites with dPE as compatibiliser produced very high and consistent tensile strength results with a very small variation of around 15 to 16 MPa for all the wood species, which indicates that dPE is equally compatible to all the wood species.

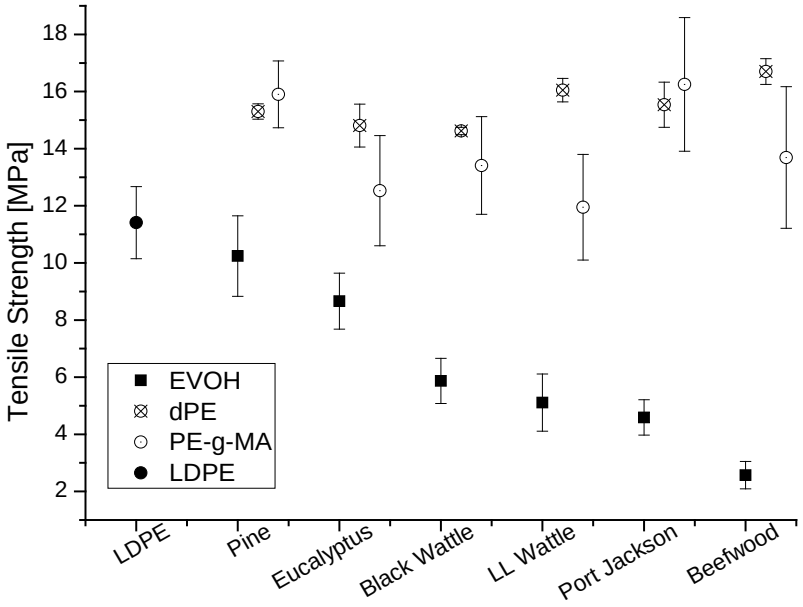

Figure 3a Tensile strength of WPCs with compatibiliser and different wood species.

Figure 3b shows the tensile strength of composites made from LDPE and the various wood species without compatibiliser at polymer/wood ratios of 70:30 and 50:50, respectively.

For all wood species a higher wood loading led to lower tensile strength and this difference was most pronounced for eucalyptus and black wattle composites.

The composites with a ratio of 70:30 showed very good tensile strength of about 14 MPa, which is comparable to the composites containing PE-g-MA and dPE as compatibilisers and better than all the composites containing EVOH as compatibiliser. The 50:50 composites showed a tensile strength between 8 and 12 MPa with fairly large variations.

These results agree with findings by Bledzki et al. (2002) and Abdelaal et al. (2012), who found that an increase in wood loading led to decreasing tensile strength in composites without compatibilisers, which could be ascribed to decrease in bonding strength between the wood and the polymer as a result of low adhesion. The tensile strength of pure LDPE was higher than that of composites made with EVOH, which means that the wood filler did not positively impact on the tensile strength, probably due to weak interphase binding through the compatibiliser. In the composites without compatibiliser the tensile strength improved with a wood loading of 30%, but decreased with increasing wood loading, which shows that the polymer matrix interacted sufficiently for lower wood loadings.

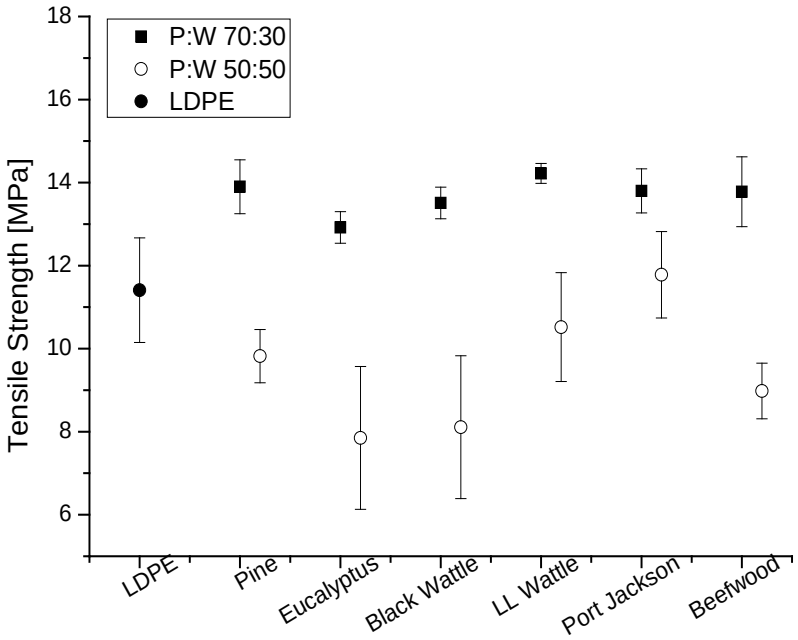

Figure 3b Tensile strength of WPCs with 30% and 50% wood content of different species without compatibiliser.

The low tensile strength of composites containing EVOH as compatibiliser compared to uncompatibilised composites show that EVOH could not improve the compatibility between the wood and polymer due to a lack of hydrogen bonding formed between the vinyl-alcohol and the hydroxyl groups of the wood particles (Kim et al. 2006). An alternative reason may be that EVOH does not interact with all parts of the polymer and therefore cancels out the positive reinforcement effects of the fibres, as described by Basson (2013). This was also highlighted by Drummond et al. (2000) who stated that EVOH facilitates only interactions between the ethylene-rich areas of the LDPE and wood. The low and significantly different tensile strength of Beefwood composites with EVOH compatibiliser may also be caused by the high pH value of the wood, since the pH of wood affects a number of properties related to the quality of wood based composites (Hernández 2013). Furthermore, the high extractive content of Beefwood may have profoundly influenced the surface chemistry of the wood (Hindi 2012; Stokke and Gardner 2003).

It can be seen from Figure 3a that wood species had a strong effect on the performance of EVOH composites. Softwood (Pine) composites performed comparable with eucalyptus composites and better than all remaining hardwood composites. This may be due to the different chemical composition of hardwoods, as highlighted in table 1. It can be seen that EVOH did not produce any gain in strength when compared with LDPE but rather decreased the strength of most composites.

The tensile strength of dPE composites is consistently high for all the wood species. The high tensile strength can be ascribed to the good interaction between the wood particles, the polymer and the compatibiliser. Since the dPE melted at the same time as the LDPE, the formation of hydrogen bonds (Ndlovu et al. 2013) with the wood particles by the carbonyl groups and the entanglement of non-polar groups with LDPE happened simultaneously and therefore a strong interface was formed, which resulted in the good tensile strength of composites with all the species. The dPE improved the compatibility between wood and LDPE aiding particle dispersion and thus provided better flowability of the hot melt, improved melt elasticity and melt strength, thereby enhancing the mechanical properties (Klyosov 2007). It is presumed that the stronger the molecular interaction between the wood and the matrix, the greater the resulting adhesive strength and the better the stress transfer. The good tensile strength of composites containing dPE may be the result of covalent bonds forming between the wood and the compatibilizer (Niska and Sanadi 2008).

PE-g-MA as compatibiliser is known to create a chemical bond between the maleated polyolefin and the wood surface, while the other end of the anhydride grafted polymer molecules physically entangles with the LDPE polymer (Niska and Sanadi 2008), which results in good tensile strength independent of the wood species. It is important to note that the molecular weight of PE-g-MA and the amount of grafted anhydride both affect the stress transfer efficiency (Niska and Sanadi 2008).

It should be noted that not only the amount of compatibiliser but also the manufacturing conditions need to be optimised to improve mechanical properties (Klyosov 2007). This can clearly be seen in the EVOH composites in Figure 3a, where EVOH may not have formed covalent bonds between the wood particles and LDPE.

The surprisingly high tensile strength of composites without compatibilisers may be attributed to the polymer matrix - LDPE, which may have somewhat thermally degraded in the compounding and moulding process and therefore acted as compatibiliser in the same way as the intentionally degraded dPE.

It is typically assumed that a larger aspect ratio of the filler particles leads to better stress transfer, which may have accounted for the good tensile strength of some of the composites without compatibilisers. The good bonding of uncompatibilised composites was the result of a good critical length of the wood particles, which improved the reinforcement effectively (Sain and Pervaiz 2008). The critical length is the length, at which maximum fibre load at the axial center of the fibre is achieved for the overall stress transfer from the matrix to the reinforcement medium.

3.3 Elongation at break

The elongation at break gives an indication for the elasticity of the composite. The elongation at break of WPCs with and without compatibiliser is shown in Figures 4a and 4b. Composites containing PE-g-MA showed with about 2 - 4% the lowest elongation at break, which was significantly lower ($p < 0.05$) from the other composites for all the wood species, with the exception of pine. In all cases the PE-g-MA composites had small standard deviations and differed little from each other. No significant difference in the elongation at break was found

between composites containing EVOH and dPE for eucalyptus, black wattle, long-leaved wattle and Beefwood. These elongations were with 6 - 10 % about three times the elongation of the PE-g-MA composites, however, with large variations. Composites with EVOH and dPE showed lower elongation at break for samples containing pine wood compared to all other wood species, which shows the effects of wood species on the elongation. Better elongation characteristics of the hardwood composites may be due to the high cellulose content of those species (Walker 2006).

The elongation at break of composites without compatibiliser is shown in Figure 4b. Composites with only 30% wood content showed higher, and significantly different, elongation at break for all the wood species compared to composites containing 50% wood. This result was similar to studies conducted by Bledzki et al. (2002) and Kim and Pal (2010) who found that increased wood loading leads to decreased elasticity. This is to be expected, as the ductility of the composites is largely imparted by the polymer. As anticipated, pure LDPE was very flexible and had a higher elongation at break than all the WPCs because of the larger chains flexibility of the LDPE chains in the amorphous regions that enables elastic deformation of the polymer when stress is applied (Ndlovu 2013). Figures 4a and 4b show the elongation at break of WPCs with and without compatibiliser and different wood species, respectively.

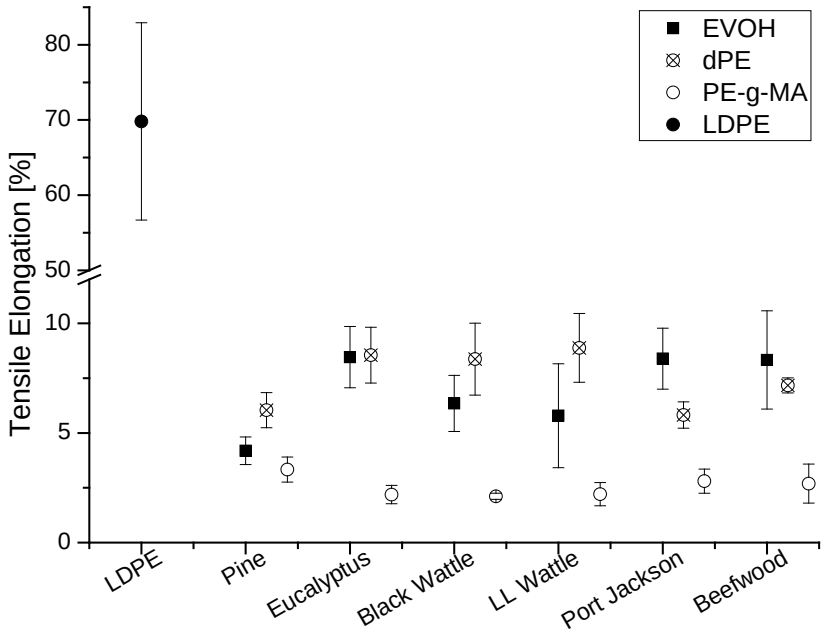

Figure 4a Elongation of WPCs with compatibiliser and different wood species

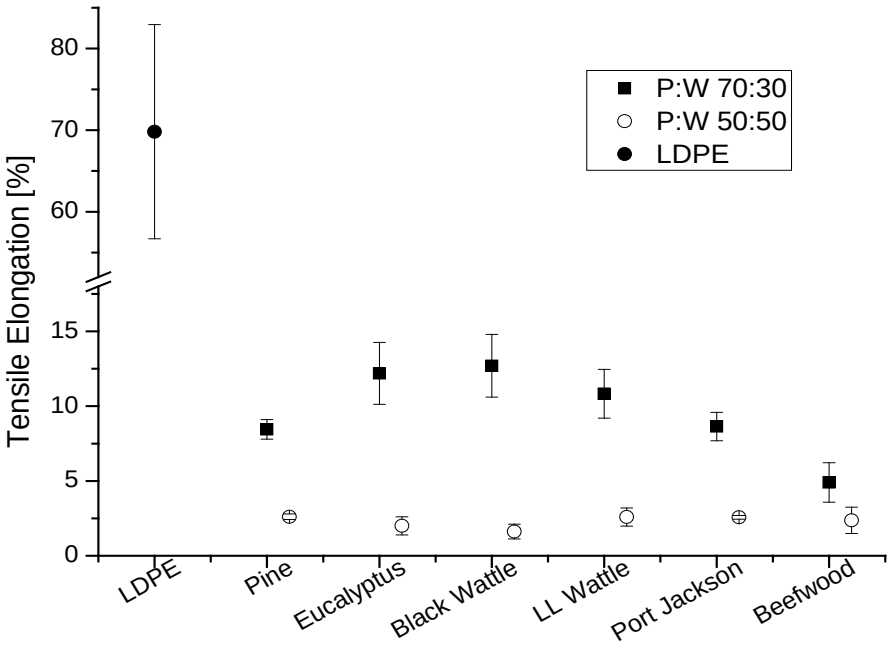

Figure 4b Elongation of WPCs with 30% and 50% wood content of different species without compatibiliser.

The elongation at break decreased with increasing wood content, which is a result of the stiffness imparted by the wood filler and further enhanced by poor interfacial adhesion (Ndiaye et al. 2011).

The elongation at break of PE-g-MA composites was similar to the 50:50 uncompatibilised composites with a low inter-sample and inter-species variation in both cases, which may be due to the fact that PE-g-MA did not contribute in any way to the ductility of the composites. On the contrary, the strong reinforcement makes the composite brittle and reduces the elasticity. The higher elongation for the 70:30 uncompatibilised composites can be assigned to the amorphous part of LDPE, which is rubbery at ambient temperatures (Bledzki and Gassan 1999).

3.4 Impact strength

The amount of energy required to break WPCs under tensile impact is given by the impact strength and the results are shown in Figures 5a and 5b. Apart from composites containing pine, no significant difference ($p > 0.05$) was found between the wood species with a large inter-sample variation. The composite containing pine and EVOH as compatibiliser absorbed the

highest energy of 10.5 J/m, while the remaining composites ranged between 6 and 8 J/m. Composites containing PE-g-MA showed the lowest variation. EVOH and dPE composites showed higher inter-sample and inter-composite variation for all wood species. The high impact strength of the Pine composites may be due to the long tracheids that absorb stress better and redistribute it into the polymer matrix (Walker 2006). It can be seen that EVOH interacts better with Pine than the hardwoods and the impact strength follows the same trend as the tensile strength. Figure 5a shows the impact strength of composites with compatibilisers.

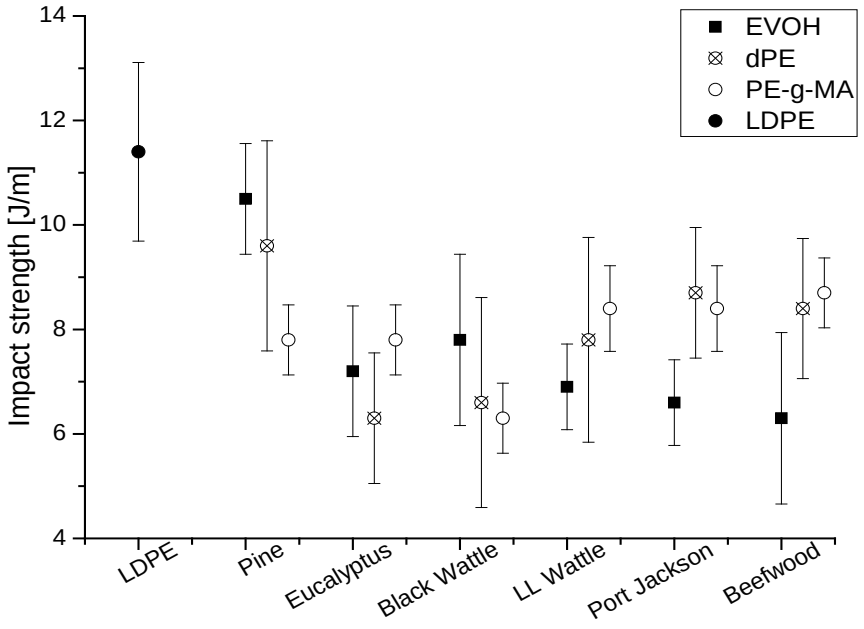

Figure 5a Impact strength of WPCs with compatibiliser and different wood species.

The impact strength of composites without compatibiliser is shown in Figure 5b. An increase in wood content led to a small decrease in impact strength for Pine, Port Jackson and Beefwood composites, although this was only significant for pine ($p < 0.05$). This is somewhat in disagreement with studies by Kim and Pal (2010), Sain and Pervaiz (2008) and Bledzki et al. (2002), who observed that an increase in wood content led to a decrease in impact strength. Pure LDPE had a higher impact strength than all the composites due to the elastic nature of the matrix. The decrease in impact strength of both compatibilised and uncompatibilised composites is the result of the wood particles, which served as stress concentration points that provided sites for crack initiation in the composite after their incorporation (Shebani et al. 2009).

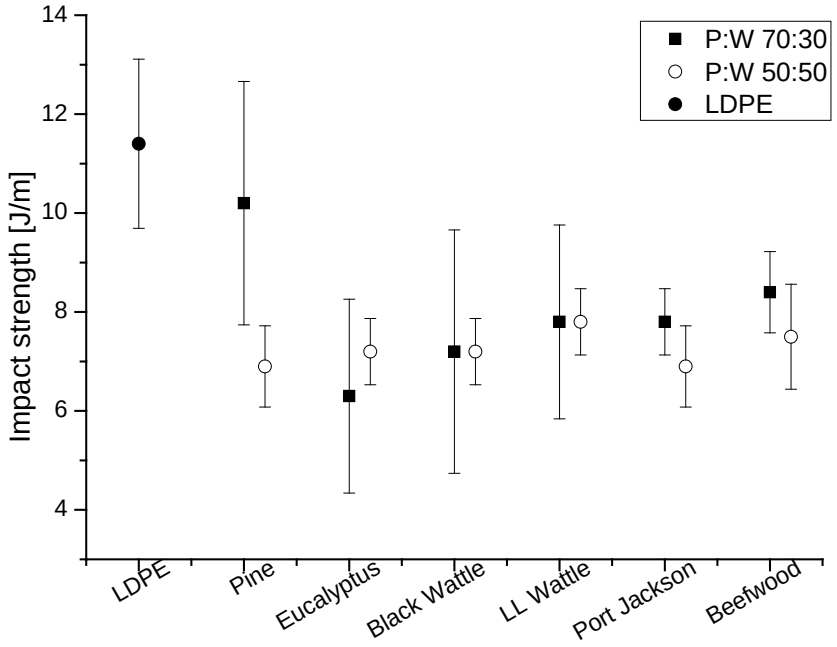

Figure 5b Impact strength of WPCs with 30% and 50% wood content of different species without compatibiliser.

Like the compatibilised composites, the impact strength of uncompatibilised composites was affected by the wood species. All the composites performed comparably, with the exception of the 70:30 Pine composites, which performed better than 50:50 composites.

3.5 Statistical analysis

ANOVA and a Tukey HSD test were applied to identify statistically significant differences between the mechanical properties of WPCs for each species group and the result presented in Table 2. The same superscript letter in a row denotes a significant difference at $p \leq 0.05$. The mean value and standard deviation (in brackets) are given.

Table 2 Mechanical properties and Tukey significance between various WPCs from six wood species based on three compatibilisers, Average (± std.)

Compatibiliser	Property	Pine	Euc	BW	LLW	PJ	BeefW
EVOH	Tensile modulus	487.61^{a} (145.35)	483.71^{b} (55.88)	445.58^{c} (95.62)	230.66^{dabc} (74.23)	480.08^{ed} (156.54)	98.87^{fabce} (19.39)
	Tensile strength	10.24^{a} (1.41)	8.66^{b} (0.98)	5.87^{cab} (0.79)	5.11^{dab} (1)	4.59^{eab} (0.62)	2.57^{fabcde} (0.48)
	Elongation	4.19^{a} (0.63)	8.46^{ba} (1.4)	6.35 (1.28)	5.79 (2.37)	8.39^{ea} (1.39)	8.33^{fa} (2.24)
	Impact	10.5^{a} (1.06)	7.2^{ba} (1.25)	7.8^{ca} (1.64)	6.9^{da} (0.82)	6.6^{ea} (0.82)	6.3^{fa} (1.64)
PE-g-MA	Tensile modulus	2289.18^{a} (331.02)	1900.54^{b} (415.4)	1528.34^{ca} (279.7)	2256^{dc} (321.09)	1354.6^{ead} (230.15)	779.76^{fabcd} (162.16)
	Tensile strength	15.9^{a} (1.17)	12.53 (1.93)	13.41 (1.71)	11.95^{da} (1.85)	16.25^{ed} (2.34)	13.69 (2.48)
	Elongation	3.33^{a} (0.57)	2.19^{ba} (0.42)	2.11^{ca} (0.14)	2.21^{da} (0.53)	2.8 (0.55)	2.69 (0.89)
	Impact	7.8^{a} (0.67)	7.8^{b} (0.67)	6.3^{cab} (0.67)	8.4^{dc} (0.82)	8.4^{ec} (0.82)	8.7^{fc} (0.67)
dPE	Tensile modulus	1812.78^{a} (523.53)	763.35^{ba} (111.9)	820.2^{ca} (333.77)	456.68^{da} (15.41)	1055.12^{ead} (172.37)	456.31^{fae} (73.36)
	Tensile strength	15.3^{a} (0.27)	14.81^{b} (0.75)	14.62^{c} (0.13)	16.05^{dbc} (0.41)	15.54^{e} (0.79)	16.7^{fabce} (0.45)
	Elongation	6.04^{a} (0.8)	8.55^{ba} (1.27)	8.37^{ca} (1.64)	8.88^{da} (1.57)	5.82^{ebcd} (0.6)	7.17 (0.34)
	Impact	9.6^{a} (2.01)	6.3^{ba} (1.25)	6.6 (2.01)	7.8 (1.96)	8.7 (1.25)	8.4 (1.34)

Table 2 highlights the differences in the same compatibiliser group due to wood species. For the tensile modulus of the EVOH based composites Pine and Eucalyptus were significantly different ($p < 0.05$) from LL wattle and Beefwood, whilst Black wattle was significantly different from LL wattle and Beefwood. LL wattle was significantly different from Port Jackson and Port Jackson was different from Beefwood. The results further show that for the three compatibiliser groups EVOH and PE-g-MA showed more (8) significant differences ($p < 0.05$)

between the species than dPE, which had seven significantly different tensile moduli.

Similarly, the tensile strength resulted in eleven significantly different results for EVOH based composites with different wood species. Composites based on dPE had six significantly different results depending on the wood species, while for PE-g-MA only two composites showed significantly different tensile strength. The elongation at break yielded three significantly different results for both EVOH and PE-g-MA based composites, while dPE had six significantly different results. Similarly, EVOH and PE-g-MA based composites yielded five significantly different results between the wood species, while dPE composites only differed between pine and eucalyptus.

A similar analysis was performed to determine the differences caused by the compatibiliser in WPC systems for each wood species. Table 3 shows the mean results of all determined properties with standard deviations in brackets. The same superscript letter in a row denotes a significant difference at $p = 0.05$.

Table 3 Mechanical properties and Tukey significance between various WPCs containing three compatibilisers based on six wood species, Average (± std.)

Species	Property	EVOH	PE-g -MA	dPE
	Tensile modulus	487.61^{a} (145.35)	2289.18^{ba} (331.02)	1812.78 (523.53)
Pine	Tensile strength	10.24^{a} (1.41)	15.9^{ba} (1.17)	15.3 (0.27)
	Elongation	4.19^{a} (0.63)	3.33^{b} (0.57)	6.04^{cab} (0.8)
	Impact	10.5^{a} (1.06)	7.8^{ba} (0.67)	9.6 (2.01)
	Tensile modulus	483.71^{a} (55.88)	1900.54^{ba} (415.4)	763.35^{cb} (111.9)
Euc	Tensile strength	8.66^{a} (0.98)	12.53^{ba} (1.93)	14.81^{cab} (0.75)
	Elongation	8.4^{a} (1.4)	2.19^{ab} (0.42)	8.55^{cb} (1.27)
	Impact	7.2 (1.25)	7.8 (0.67)	6.3 (1.25)
	Tensile modulus	445.58^{a} (95.62)	1528.34^{ba} (279.7)	820.2^{cb} (333.77)
BW	Tensile strength	5.87^{a} (0.79)	13.41^{ba} (1.71)	14.62^{ca} (0.13)
	Elongation	6.35^{a} (1.28)	2.11^{ba} (0.14)	8.37^{cb} (1.64)
	Impact	7.8 (1.64)	6.3 (0.67)	6.6 (2.01)
	Tensile modulus	230.66^{a} (74.23)	2256^{ab} (321.09)	456.68^{cb} (15.41)
LL W	Tensile strength	5.11^{a} (1)	11.95^{ba} (1.85)	16.05^{cab} (0.41)
	Elongation	5.79^{a} (2.37)	2.21^{ba} (0.53)	8.88^{cab} (1.57)
	Impact	6.9 (0.82)	8.4 (0.82)	7.8 (1.96)
	Tensile modulus	480.08^{a} (156.54)	1354.6^{ba} (230.15)	1055.12^{ca} (172.37)
PJ	Tensile strength	4.59^{a} (0.62)	16.25^{ba} (2.34)	15.54^{ca} (0.79)
	Elongation	8.39^{a} (1.39)	2.8^{ba} (0.55)	5.82^{cab} (0.6)
	Impact	6.6^{a} (0.82)	8.4^{ba} (0.82)	8.7^{ca} (1.25)
	Tensile modulus	98.87^{a} (19.39)	779.76^{ba} (162.16)	456.31^{cab} (73.36)
BeefW	Tensile strength	2.57^{a} (0.48)	13.69^{ba} (2.48)	16.7^{cab} (0.45)
	Elongation	8.33^{a} (2.24)	2.69^{ba} (0.89)	7.17^{cb} (0.34)
	Impact	6.3^{a} (1.64)	8.7^{ba} (0.67)	8.4 (1.34)

For both tensile modulus and strength, a statistically significant difference ($p < 0.05$) was found between EVOH and PE-g-MA, as well as EVOH and dPE composites containing pine. The elongation at break was significantly different for EVOH and dPE and PE-g-MA and dPE composites, while the impact strength differed significantly for EVOH and PE-g-MA.

In the case of eucalyptus, the tensile modulus showed significant differences between EVOH and PE-g-MA, and between PE-g-MA and dPE composites, while all the three compatibilisers

showed significant differences in tensile strength. Differences in the elongation at break were found between EVOH and PE-g-MA as well as PE-g-MA and dPE composites and the impact strength was not statistically different for all three compatibilisers. For Black Wattle significant differences were found between EVOH and PE-g-MA, then PE-g-MA and dPE for both tensile modulus and elongation at break, while the tensile strength differed significantly between EVOH and PE-g-MA, and EVOH and dPE, respectively.

Composites made with Long-leaved wattle showed significant differences in tensile modulus between EVOH and PE-g-MA, and PE-g-MA and dPE. All the three compatibilisers were significantly different from each other in terms of tensile strength and elongation at break and no significant difference was found for the impact strength. For Port Jackson, significant differences following the same trend - between EVOH and PE-g-MA, and EVOH and dPE - were recorded for tensile modulus, tensile strength and impact strength and significant differences existed between all compatibilisers for the elongation at break. For WPCs containing Beefwood, all compatibilisers performed significantly different in tensile modulus and tensile strength. However, for the elongation at break, differences were observed between EVOH and PE-g-MA, as well as PE-g-MA and dPE. For impact strength only a difference between EVOH and PE-g-MA was observed. In summary Beefwood and Port Jackson showed more (9) significant differences between the compatibilisers than the other species, with Black Wattle having the least (6) significant differences.

4 Conclusions

The potential of wood reinforced polymer composites for use in industrial applications significantly depends on their mechanical properties. In this study, the effects of different compatibilisers, namely EVOH, PE-g-MA and dPE on WPCs containing different wood species were investigated. These wood species are – apart from Pine- all hardwoods and not currently used for WPC production. Composites with PE-g-MA as compatibiliser showed the highest tensile modulus for all wood species. EVOH composites were less rigid with a low tensile modulus for all the wood species. The tensile modulus of composites without compatibiliser increased significantly with increased wood loading for most of the species, thus more wood provided more rigid composites, which require higher stress to break.

The composites containing EVOH did not show any gain in strength when compared to pure LDPE and the other compatibilisers, but rather decreased composite strength. Composites containing PE-g-MA had generally a higher tensile strength and were less sensitive to the wood species. Composites containing dPE as compatibiliser had a consistently high tensile strength with the lowest variation between wood species. An increase in wood loading led to a decrease in tensile strength in composites without compatibiliser, but the tensile strength of composites containing 30% wood was comparable to the tensile strength of WPCs containing compatibiliser.

Composites with dPE compatibiliser had the highest elongation at break for most of the wood species. Composites containing PE-g-MA had the lowest elongation at break for most of the species, which means that they are more brittle than the composites made with the other compatibilisers. An increase in wood loading led to a decreased elongation at break in composites without compatibilisers, as the wood particles do not contribute to elasticity. For the impact strength, pine composites performed better than the hardwood composites, which can probably be explained by the long tracheids in softwoods, compared to the shorter fibres in hardwoods.

The mechanical properties of wood-plastic composites are highly formulation dependent. In addition to the quality and amount of matrix polymer, the wood and compatibiliser play a significant role with regards to the final composite properties. For example, the good tensile strength of PE-g-MA and dPE composites makes them suitable for WPC items that require high tensile strength such as construction components like door and window frames, doors, decking and outdoor furniture. On the other hand, the good impact strength of EVOH composites makes them suitable for railings, automotive components, military wares, floor panels, and walk ways, and playground furniture. Various products may also be produced from a combination of the compatibilisers.

In conclusion, this study shows that the invasive wood species that were studied can be incorporated into WPCs, as the properties of the final products differ little - if the correct compatibiliser is chosen. AIS represent a source of renewable material with attractive properties for WPCs as they are inexpensive, unexploited and available in abundance. Therefore, incorporating them into WPCs as wood fillers can provide substantial value adding to a waste material, whilst producing products with good performance properties. Furthermore, thermally degraded LDPE presents a new and inexpensive compatibiliser that can replace traditionally used expensive compatibilisers, in many cases with superior properties.

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Conflict of interest

The authors declare that they have no conflict of interest.

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Chapter Seven

Conclusions

WPCs are a combination of a thermoplastic matrix and ligno-cellulosic filler particles. Their use has experienced a steady growth since the 1990s and is projected to continue to increase in the coming decades (Clemons 2002). Currently, commercial WPC products are increasingly replacing many products for various applications, especially the construction and automobile related areas (Yeh et al. 2009; Schwarzkopf and Burnard 2016). Among the lignocellulosic filler particles, wood is the most common and abundantly available low-cost natural fibre that has been used as reinforcement in a thermoplastic matrix, which consists mostly of polyolefins (Bledzki et al. 2002). The wood fibres often come from side streams, such as sawdust generated while manufacturing lumber, recovered wood products, logging trimmings and small diameter trees (Clemons and Stark 2007; Schwarzkopf and Burnard 2016).

The surface of wood fibres is predominately polar due to the presence of hydroxyl and other polar groups on the cellulose and hemicellulose backbone, whilst polyolefins are nonpolar. This leads to incompatibility between the two components, which may result in limited adhesion (Spiridon 2014; Schwarzkopf and Muszynski 2015). This problem is typically overcome with the addition of a third component, a compatibiliser with different functional groups, of which one reacts with the hydroxyl groups of the wood and the other attaches to the polymer (Salemane and Luyt 2006).

The physical and mechanical properties of WPCs depend strongly on the interfacial adhesion between the wood and polymer matrix (Farsi 2012). In this study the interfacial adhesive forces acting in various LDPE-wood composites were studied with CFM and related to the physical and mechanical properties. The WPCs consisted of LDPE with wood fillers from six invasive species and three different compatibilisers.

The first stage of the research established the basic concept and fundamentals of WPCs, their main components and how they interact with each other. The adhesive properties between the components depend on interatomic and intermolecular surface forces, such as van der Waals forces, electrostatic forces, chemical forces and capillary forces (Zhao et al. 2003). There are two main interaction forces, which are short range forces and long range forces (Israelachvili 2011). Short range forces originate from chemical bonding, whilst long range forces originate

from physical attraction due to the formation of weak van der Waal's bonds, or hydrogen bonds between the two substrates (Kim and Pal 2010). CFM has the ability to create 3D, high resolution images of the surface morphology and as well as a map of the interaction forces and is therefore very suitable to characterise WPCs. A strong interfacial bond effectively transfers load from the matrix to the fibre and hence improves the mechanical performance of the composite (Ndiaye et al. 2011). When adhesion is poor in WPCs, wood fibres act mainly as filler in the matrix and the mechanical properties are typically inferior. When the adhesion is adequate, the wood fibres work as reinforcement in the matrix (Baillie 2004). AFM can be used to characterise the surface structure, as well as chemical functionalities of the different components and localise and to a degree quantify functional groups and therefore give an indication of their adhesive forces on a molecular scale.

In WPCs, the efficiency of stress transfer from the polymer matrix to the wood filler is affected by the surface properties of both materials. In order to detect the distribution of relevant functional groups, the tip-surface interaction forces between different wood species and AFM tips modified with different compatibilisers were mapped to analyse the varying compatibility. Wood species differ in their chemical composition, which obviously affects the type and amount of chemical functional groups on the surface (Stolf and Lahr 2004) to which compatibilisers can bind.

It was shown that EVOH was very sensitive to the wood species, whereas PE-g-MA showed comparable results for all species. The force maps obtained on Pine and Beefwood clearly showed that the amount of binding sites for EVOH differed on the two wood species, whereas the amount of binding sites for PE-g-MA seemed fairly evenly distributed on both wood species. The histograms of the adhesive forces detected on the cell wall surfaces showed that distribution varied with the species and compatibiliser system used. EVOH had more potential binding sites on Pine than on Beefwood, shown by the amount of high value adhesive forces. It was concluded that not all compatibilisers work equally well with different wood species, because they differ significantly in their surface characteristics. This means that great care needs to be taken in the choice of WPC components when wood species other than the conventional softwoods are to be used for WPC production. The study also demonstrated the possibility to map the spatial distribution of chemically distinct functional groups on the surface of wood fibres with functionalised AFM tips.

In order to understand how well the three components of WPCs adhere to each other, chemically functionalised tips were used to quantify the adhesive force between the compatibiliser coated AFM tips, the polymer and the six different wood substrates and the results were correlated to macroscopic WPC properties in an attempt to understand the mechanical properties, as well as to determine the feasibility to use alien invasive wood species for the production of WPCs and to determine the most suitable compatibiliser.

The measured MCs of the WPCs were all higher than those determined in commercial WPCs, such as Geodeck boards, which have an MC of 1.7 % (Klyosov 2007). The high MC of EVOH composites negatively affected and lowered tensile strength of the final WPC. The EVOH composites were found to have good tensile strength with Pine and Eucalyptus wood, however, EVOH proved to be very sensitive to the wood species and did not perform well with the other wood species. Composites containing PE-g-MA had higher tensile strength and the results varied less with the wood species. Composites containing dPE as compatibiliser had a high tensile strength for all investigated species and the values were comparable to the WPCs containing PE-g-MA. The measured densities compared very well to the densities of commercial products, such as Boardwalk, Trex, Monarch and Rhino Deck WPCs (Klyosov 2007). The tensile strength of the WPCs determined in the study compared well with commercial WPCs, for example, products of TimberTech, GeoDeck, Trex, EverX and Timberlast, which have tensile strength values of 8-13 MPa (Klyosov 2007). However, the results were difficult to relate, as many factors, such as the wood species, MC, density, compatibiliser and processing method affect the performance of the final product. The study showed that invasive wood species may be incorporated into WPCs, if the correct compatibiliser is chosen. dPE proved to be the best choice, as it had the lowest sensitivity to the wood species and yielded WPCs with good mechanical strength.

The final chapter of the study focused on the mechanical properties of WPCs made from LDPE, six invasive wood species and three different compatibilisers. The tensile modulus, tensile strength, elongation at break and impact strength were analysed.

WPCs with PE-g-MA as compatibiliser showed the highest tensile modulus for all wood species. EVOH composites were less rigid with a low tensile modulus for all the wood species. The tensile modulus of composites without compatibiliser increased significantly with increased wood loading for most of the species and more wood led to more rigid composites, which

require higher stress to break.

WPCs containing EVOH were found to have reasonably good tensile strength when Pine and Eucalyptus were used as wood fillers. WPCs containing PE-g-MA had generally a higher tensile strength and were less sensitive to the wood species. WPCs containing dPE as compatibiliser had a consistently high tensile strength with the lowest variation between wood species. An increase in wood loading led to a decrease in tensile strength in composites without compatibiliser, but the tensile strength of composites containing 30% wood was comparable to the tensile strength of WPCs containing compatibiliser.

WPCs with dPE compatibiliser had the highest elongation at break for most of the wood species. Composites containing PE-g-MA had the lowest elongation at break for most of the species, which means that they are more brittle than the composites made with the other compatibilisers. An increase in wood loading led to a decreased elongation at break in composites without compatibilizers, as the wood particles did not contribute to elasticity. For the impact strength, Pine composites performed better than the hardwood composites, which can be explained by the long tracheids in softwoods, compared to the shorter fibres in hardwoods.

The incorporation of PE-g-MA and dPE compatibilisers improved adhesion and thus enhanced the tensile properties of the composite. The good tensile strength of PE-g-MA and dPE composites makes them suitable for products that require high tensile strength, such as door and window frames, doors, decking and outdoor furniture. On the other hand, the good impact strength of EVOH composites makes them suitable for railings, automotive components, military wares, floor panels, and walk ways and playground furniture. Various products may also be produced from a combination of the compatibilizers.

In conclusion, the study showed CFM can be used to characterise the surface structure and chemical functionalities of the different components and localise and quantify functional groups and therefore give an indication of potential binding sites on a molecular scale. Finally, it was shown that the studied invasive wood species can be incorporated into WPCs, if the correct compatibiliser is used. This will provide substantial value adding to a waste material, while at the same time resulting in products with good performance.

Furthermore, thermally degraded LDPE presents a new and inexpensive compatibiliser that can replace conventionally used expensive compatibilisers, in many cases with superior properties. dPE can be sourced from recycled material, just as the matrix polymer.

At the end of the study, the following novelty was established:
AFM tips were functionalised with molecules terminating with dPE and PE-g-MA compatibilisers. The study quantified the adhesion between wood cell wall surfaces and WPC compatibilisers. The study also mapped the spatial distribution of chemically distinct functional groups on the cell wall surface of wood with functionalised compatibiliser tips. From this study, the feasibility of using AIS especially beefwood, port Jackson and long-leaved wattle as fillers for the production of WPCs. Finally, a new methodology was developed by quantitatively correlating macroscopic properties to microscopic properties.

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Appendix A

Declaration by candidate and co-authors

Chapter 3

With regards to Chapter 3 (Characterisation of the Interfacial Adhesion of the Different Components in Wood-Plastic Composites with AFM), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution
Reviewed literature and carried out pilot study	85%
Conceptualised and wrote the paper	

The following co-authors contributed to Chapter 3

Name	E-mail address	Nature of contribution	Extent of contribution
A. Van Reenen	ajvr@sun.ac.za	- Provided advice as co-supervisor - Contributed to editing of paper	5%
M. Meincken	mmein@sun.ac.za	- Provided advice as main supervisor - Contributed to editing of paper	10%

Chapter 4

With regards to Chapter 4 (Localisation and quantification of potential binding sites for compatibilisers on soft- and hardwood in wood-plastic composite systems), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution
Reviewed literature	85%
Performed all experiments	
Data analysis	
Conceptualised and wrote the paper	

The following co-authors contributed to Chapter 4

Name	E-mail address	Nature of contribution	Extent of contribution
A. Van Reenen	ajvr@sun.ac.za	- Provided advice as co-supervisor - Contributed to editing of paper	5%
M. Meincken	mmein@sun.ac.za	- Provided advice as main supervisor - Contributed to editing of paper	10%

Chapter 5

With regards to Chapter 5 (Chemical Force Microscopy Analysis of Wood Plastic Composites Produced from different Wood Species and Compatibilisers), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution
Reviewed literature	80%
Performed all experiments	
Data analysis	
Conceptualised and wrote the paper	

The following co-authors contributed to Chapter 5

Name	E-mail address	Nature of contribution	Extent of contribution
K. Raatz	16228065@sun.ac.za	- Preparation of WPC samples	5%
A. Van Reenen	ajvr@sun.ac.za	- Provided advice as co-supervisor - Contributed to editing of paper	5%
M. Meincken	mmein@sun.ac.za	- Provided advice as main supervisor - Contributed to editing of paper	10%

Chapter 6

With regards to Chapter 6 (Mechanical properties of wood plastic composites made from various wood species with different compatibilisers), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution
Reviewed literature	85%
Performed all experiments	
Data analysis	
Conceptualised and wrote the paper	

The following co-authors contributed to Chapter 6

Name	E-mail address	Nature of contribution	Extent of contribution
A. Van Reenen	ajvr@sun.ac.za	- Provided advice as co-supervisor - Contributed to editing of paper	5%
M. Meincken	mmein@sun.ac.za	- Provided advice as main supervisor - Contributed to editing of paper	10%